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EVALUATION OF SPATIAL AND TEMPORAL PATTERNS OF PRIORITY CONTAMINANTS IN SEDIMENTS OF THE HURON-ERIE CORRIDOR

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EVALUATION OF SPATIAL AND TEMPORAL PATTERNS OF PRIORITY CONTAMINANTS IN SEDIMENTS OF THE HURON-ERIE CORRIDOR

By

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Evaluation of spatial and temporal patterns of priority contaminants in sediments of the Huron-Erie Corridor

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DECLARATION OF CO-AUTHORSHIP

I hereby declare that this thesis incorporates material that is result of joint research, as follows: Chapters 2 and 3 of this thesis will be published as co-authored, peer-reviewed journal articles. Chapter 2 is being prepared for submission to Chemosphere with co-authorship with Alice-Ggicak-Mannion and Ken Drouillard. Chapter 3 is being prepared for submission and will include co-authors: Ewa Szalinska, Alice Grgicak-Mannion, Kerry McPhedran, Ken G. Drouillard, Ted Briggs and G. Douglas Haffner. The latter co-authors contributed to the previous studies which generated data utilized in Chapter 3, contributed to funding support and editorial review of works completed. Alice Grgicak-Mannion, Kerry McPhedran and Ken G. Drouillard contributed to the experimental design and sampling of portions of the 2013-2014 survey data used in both chapters. I contributed to the sample collection of samples from St. Clair River and Lake St. Clair in the 2013-2014 survey used in Chapter 2 and 3, the complete analytical chemistry workup, database generation and quality assurance/quality control aspects of the 2013-2014 survey data. I also led the data interpretation and writing of all chapters in this thesis with editorial contributions contributed by the above stated co-authors.

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ABSTRACT

This thesis examined spatial and temporal patterns of sediment contamination within the Huron-Erie Corridor which consists of two Areas of Concern, the St. Clair River and the Detroit River. Stratified random sampling designs of surficial sediment samples, both current (2013-2014) and past (1999-2005), were used to evaluate contamination patterns as well as trends observed in time. Chapter 2 focused on Mercury (Hg) concentrations to evaluate a geospatial clustering technique (Getis-Ord) neighbourhood parameter and contrast three different methods for Getis-Ord implementation (fixed distance, inverse distance and user defined matrix procedures). Validation exercises indicated that the fixed distance approach yielded the poorest results and generated inaccurate representations of hot and cold spots within the corridor. The inverse distance and user defined matrix approaches yielded similar validation efficacy, with the user defined matrix generating larger hot zone regions that compared best to previously described spatial patterns described in the literature. Chapter 3 focused on 13 priority contaminants to evaluate spatial and temporal patterns of sediment contamination. Data reduction by principle components analysis revealed 2 major contaminant groups; group 1 chemicals included PCBs, PAHs, transnonachlor, DDE and several metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) and group 2 chemicals was highlighted by HCB and OCS. Total Hg did not load strongly onto any PCA axis but given its importance as a priority chemical, it was evaluated separately. Spatial patterns were much stronger than temporal patterns, with the latter confounded by sampling resolution differences between survey periods. Group 1 chemicals were enriched primarily in the U.S. jurisdiction of the Detroit River. Group 2 chemicals and Hg were enriched in localized areas in Canadian waters of the St. Clair River, variable locations in Lake St. Clair and in U.S. downstream sections of the Detroit River.

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CHAPTER 1 – GENERAL INTRODUCTION

1.1 – General Introduction

Agricultural and industrial processes coupled with rising human populations and the spread of globalization have led to sediment contamination being found in almost all water systems worldwide (Reynoldson and Zarull, 1989). One of these freshwater areas under particular environmental stress is the Laurentian Great Lakes (Grapentine, 2009). As human impacts on the environment continue to grow, the need for the management of ecosystem and water quality of one of the largest freshwater areas in the world becomes increasingly crucial (Cairns Jr. et al., 1993; Nobi et al., 2010). Both Canada and the United States have recognized this importance and beginning in 1972 the Great Lakes Water Quality Agreement (GLWQA) was signed. There have since been 42 Areas of Concern (AOCs) designated within the Great Lakes as a result of one or more designated impaired beneficial uses as specified by the International Joint Commission (IJC, 1987).

Within the Laurentian Great Lakes is the Huron Erie Corridor (HEC) consisting of the St. Clair River, Lake St. Clair and the Detroit River. At 157 km in length, it is the main connecting waterway between Lake Huron and Lake Erie. This system is particularly complex, consisting of two riverine systems, one deltaic and one lake system(Szalinska et al., 2007). The corridor serves as the international border between the United States and Canada and runs through agricultural, along with highly urbanized and industrialized areas resulting in a complex history of contamination from a variety of sources (Point, Non Point, Upstream) (Szalinska et al., 2006). Both the St. Clair River and

the Detroit River are designated Great Lakes Areas of Concern (AOCs), with two additional AOCs the Clinton River and the Rouge River flowing into the system. Both the Detroit River and St. Clair River Remedial Action Plans identified upwards of 10 beneficial use impairments each including but not limited to degradation of benthos, loss of fish and wildlife habitat, degradation of fish and wildlife populations, restrictions on fish consumption and beach closings (DRCCC, 2009; Szalinska et al., 2007; US EPA, 2013a, 2013b). There has been widespread monitoring, mainly within specific reaches of the corridor, throughout the past 30 years(Szalinska et al., 2007; US EPA, 2013a).

A beneficial use impairment (BUI) is defined as a use that has been compromised due to a change in chemical, physical or biological integrity within a system. There are a total of 14 standardized use impairments used and assessed across the AOC's (IJC, 1987). The Detroit River was allocated a 15th beneficial use impairment with respect to exceedances of water quality standards. Sediment contamination itself is a factor directly related to a number of BUIs identified in the HEC. Accumulation of a variety of pollutants in sediments led to the degradation of ecosystem health, accumulation of contaminants in tissues of benthic organisms and fishes, along with drinking water restrictions and restrictions of dredging activities(Richman and Milani, 2010). Due to this, the evaluation of sediment chemistry has long been used to monitor contaminant levels and their respective locations throughout the HEC. Historically, the St. Clair River and Detroit River have been of greater focus in studies (Oliver and Bourbonniere, 1985; Richman and Milani, 2010; Szalinska et al., 2006) though more recent efforts have been

adapted to studying Lake St. Clair along with the corridor as a system (Szalinska et al., 2007).

A number of complex factors govern the spread of contaminants within large systems such as the HEC. A contaminant is defined as a chemical enriched by anthropogenic activities, though it may not necessarily cause harm. Contaminants through initial release are transported by being a) dissolved into the water phase, b) partitioned/adsorbed onto particles and then transported via suspended sediments, or c) by the movement of the bedload, i.e. downstream transport of sediments along the river bottom(Drouillard et al., 2006; Lau et al., 1989). Contaminants associated with scavenged particles have been shown to be deposited and accumulate in areas where the water current can no longer sustain particle transport (Szalinska et al., 2011). The HEC consists of altered flow in channels and variable deposition zones (both nearshore and deltaic) that contribute to a high variation of particle size distributions, and sediment consolidation and composition differences(Szalinska et al., 2013). Differences in particle size, organic carbon and mineral content can influence the concentration and type of contaminants that can be found to load or accumulate together. Organic matter has been shown to retain organic contaminants (Hawker and Connell, 1988) while the finer clay fraction has been observed to preferentially retain metal and metalloid particles (Golterman, 2004). These geochemical variables, coupled with diverse input/source locations, contribute to high heterogeneity of contaminant patterns in sediments beyond what is observed compared to more homogeneous environmental media such as air or water.

Current and historical anthropogenic activities has also been found to influence the dispersion and location of contaminants found in sediments (Szalinska et al., 2011). The HEC being a major trading and shipping route is one of the most heavily industrialized and environmentally altered areas in the Great Lakes (Szalinska et al., 2011). There is variation in the stresses placed along the corridor, with specific zones exhibiting greater concentration of industry than others. The St. Clair River has a heavy industry presence found on the Upper/Midstream Canadian side, whereas the Detroit River is governed by two large metropolitan areas, Detroit and Windsor, as well as industry along the U.S. midstream portion. Anthropogenic sources associated with the above locations were shown by Szalinska et al., 2011 to have a greater impact on the distribution patterns of contaminants than the geochemical sorting processes in sections of the HEC. The localized areas of contaminants identified in the study corresponded with the areas of industry leading to location and sources as a justifiable factor in contaminated sediment distribution patterns within the HEC.

The long history of contamination throughout the HEC and the AOC designation led to the implementation of Remedial Action Plans (RAP). These were put into place to provide goals to improve the state of the system over time. The extent of sediment contamination was one of the main focuses of the clean-up effort outlined in the RAP (Zarull et al., 2001). Sediment contamination has been intensively studied throughout the corridor over the last thirty years with earlier studies identifying problem areas within the river systems (Besser et al., 1996; Hamdy and Post, 1985; Pugsley et al., 1985). Midstream and downstream Detroit River sediments in areas such as the Trenton

channel showed elevated concentrations of multiple contaminants. Additionally, the identification of high levels of historical contaminants downstream of Sarnia's Chemical Valley on the Canadian side (Szalinska et al., 2007) led to large-scale sediment clean-up activities. Since 1993 over 1 million cubic meters of contaminated sediments have been removed from the Detroit River at a cost of over 150$ million dollars (U.S.) (Hartig et al., 2004). There has been over $200 million (U.S.) spent on the improvement of sewage treatment and wastewater facilities in both countries. Additionally, the remediation of roughly 14,000 cubic meters of contaminated sediments was completed by Dow Chemical adjacent to their property in the St. Clair River (US EPA, 2013b).

These clean-up activities have led to concentration decreases observed through post monitoring activities, though the extent of such actions to the system recovery as a whole has not been demonstrated since post-mitigation monitoring work has been typically constrained to the area of clean up (Szalinska et al., 2013). Still, through the extensive work completed on the system over time there have been noticeable improvements, with 5 BUIs removed in the St. Clair River and 2 BUIs in the Detroit River (US EPA, 2013a, 2013b).

Though clean-up efforts and monitoring have resulted in significant improvements with time the studies that were taking place were failing to provide the context of improvement at the corridor wide scale (Szalinska et al., 2013). There were two main problems with the studies taking place. These studies were often biased towards locations of point sources or previously identified areas of degradation (Haffner et al., 2000; Szalinska et al., 2006). This could significantly misrepresent the entire system's

health. Beyond just localization and time events, studies were generally structured to evaluate a few specific target contaminants or problems in that area. Studies were not structured to be representative of each other in a timely and spatially relevant sequence that could account for historical trends and system-wide changes (Haffner et al., 2000; Szalinska et al., 2006).

A structured, large-scale study implemented to answer the question of whether the state of the system was improving for the Detroit River AOC was completed in 1999 (Drouillard et al., 2006; Szalinska et al., 2006). That survey sampled 150 stations within the boundaries of the AOC according to a stratified random geostatistical design. Each sample location generated bulk sediment chemistry data for metals and priority organic pollutants to serve as a baseline for contaminant levels within the river. This study was set apart from previous studies in two main factors: 1) the extent of sediment chemistry parameters analyzed and 2) the sampling design and implementation of a random stratified sampling approach which encompassed all waters within the AOC boundary.

The sediment chemistry parameters implemented above included grain size, moisture content, total organic carbon, and a suite of contaminants that included metals, PCBs and PAHs previously identified as priority contaminants within the HEC. This allowed a complete dataset which can lead to understanding sediment dynamics and to determine which contaminants were grouping together in specific locations (Drouillard et al., 2006; McPhedran et al., 2016; Szalinska et al., 2006). The sampling design utilized a stratified random sampling approach. With 150 sample locations, this design also provided for equal dispersion of samples across the river length in U.S. and

Canadian waters, but also limited sampling of sediments in the dredged navigational channels. Clustering was taken into account by ensuring that adjacent sample locations were no closer than 300 m to one another. The survey helped to identify contaminated areas, evaluate the state of the system and helped to show the differences in environmental health of the river through the comparison of sediment chemistry results with Sediment Quality Guidelines (SQGs). Following the 1999 Detroit River study, the sampling design was expanded for an additional survey in 2004 that encompassed the HEC with 108 sites sampled throughout its waters (Szalinska et al., 2007). This established the first survey for the St. Clair River and Lake St. Clair and allowed a contrast between contaminated systems and the different AOCs of the HEC. Additional sediment surveys were completed within the Walpole Island Delta (2005, 2012) encompassing a total of 87 sites, and in the Detroit River in 2008/09 covering 65 sites (Szalinska et al., 2013).

Technological advances have changed the way we map, design and evaluate the distribution environmental attributes. The use of Geographic Information Systems (GIS) make geostatistical analysis of large-scale datasets easier and more manageable. Recently, following the successes of the large-scale surveys throughout the corridor, there has been some work to develop hazard zones of contaminants using GIS software. The study by Szalinska et al., 2013 applied GIS approaches to interpret temporal and spatial changes observed on the 1999 and 2008/09 Detroit River studies that included mass balance, along with regional and local geospatial assessment techniques. One novel method applied was the use of the Getis-Ord Gi* statistic. The Getis-Ord Gi*

Statistic measures how spatial autocorrelation varies locally over a study area and computes a new statistic for each data point that takes into consideration weighted concentrations at individual sampling stations and places these into the context of the system-wide mean concentration (ESRI, 2016). The method evaluates the degree to which a point and its neighbours exhibit similarly high or low values in contamination compared to the system mean concentration for a given contaminant. Output values are defined as z-scores, with high positive values indicating a hotspot (i.e. distance weighted concentrations significantly elevated above the system mean), whereas negative values indicate a cold spot (locations having distance weighted concentrations significantly lower than the system mean). The method allows for the localization of hot and cold spot zones within the Detroit River by identifying clusters of sites that are above and below the mean contamination for the system. The study coupled hotspot analysis with mass balance and principal component analysis techniques in order to evaluate if changes in the overall contamination, regional contamination and localized hot/cold spots have been observed in the Detroit River over the previous ten-year period. This was the first step in taking baseline surveys to evaluate if the system was improving over time.

The implementation of large-scale studies across multiple survey years as demonstrated within the Detroit River has allowed for greater understanding of the state of this Area of Concern. Advanced geospatial analysis techniques implemented in the Detroit River have begun to characterize temporal changes in contaminant dispersion. The techniques observed need to be further improved upon and

implemented at the corridor scale. Furthermore, understanding the interactions and groupings of multiple contaminants at sampling sites can help to understand where multi-contaminant hotspots exist that can further shed light into potential source regions and sediment-associated toxicity.

1.2 – Thesis Objectives

This thesis will address a comprehensive geospatial analysis of priority pollutants in sediments distributed in the Huron Erie corridor. The research has the following objectives:

Chapter 2 of this thesis assessed the most appropriate method for applying the Getis-ord statistic in the Huron-Erie Corridor. This objective was addressed by focusing on total mercury as a priority contaminant due to its anthropgenic nature and well defined history of study in the Huron-Erie Corridor. Previous application of the Getis-Ord statistic to the Detroit River (Szalinska et al. 2013) utilized a fixed distance approach to define which sample neighbours have influence for a given location. However, this approach considered all points within the defined distance as equal and did not weight them based on their actual physical connectivity to one another. Furthermore, it did not consider that directional water flow within the connecting channels places constraints on sediment mixing probabilities and therefore could lead to inappropriate allocation of hot and/or cold spots within the system as a result of incorporating neighbor sampling sites in the weighted Getis-Ord statistic. This thesis research was developed to compare and contrast the most appropriate of three Getis-Ord approaches (fixed distance,

inverse distance weighting and a new user defined matrix that considers hydraulic and island barriers) to describe mercury contamination in sediments of the Huron-Erie corridor. It was hypothesized that methods that account for distance weighting and/or account for physical and hydraulic barriers will provide a more accurate estimate of hot and cold regions.

Chapter 3 of this thesis was developed to provide the first temporal assessment of multi-pollutant sediment contamination at the corridor scale within the HEC. Building from the methodology generated in Szalinkska et al. (2013) applied to the Detroit River and incorporating the results of Chapter 2 on Getis-Ord statistic optimization, Chapter 3 of this thesis evaluated the mass balance, regional, and local changes in sediment contamination for priority pollutants in the HEC from 1999 to 2014. This chapter tested whether or not changes in the magnitude and location of priority contaminants in sediments have occurred within the system over the past decade and whether similar patterns of change are apparent across multiple contaminants. It was hypothesized that contamination will have decreased in specific reaches of the corridor such as the Detroit River U.S. side and St. Clair River Canadian side due to remediation activities designed to mitigate legacy deposits. It was expected that zones of low contamination would remain relatively stable as previous studies have shown (Szalinska et al., 2013).

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CHAPTER 2 – APPLICATION OF THE GETIS-ORD GI* STATISTIC TO UNCOVER LOCAL PATTERNS OF ENRICHED AND BASELINE MERCURY CONTAMINATION IN SEDIMENTS OF THE HURON-ERIE CORRIDOR

2.1 – Introduction

Agricultural and industrial processes coupled with rising human populations have led to the global problem of sediment contamination in freshwater systems (Reynoldson and Zarull, 1989). This is particularly evident in the Laurentian Great Lakes which provide 18% of the world's surface freshwater and exhibit strong gradients in sediment pollution related to population density, patterns of land use and historic pollution (Grapentine, 2009). Under the Great Lakes Water Quality Agreement (GLWQA), there are 35 currently active (non-delisted) Areas of Concern (AOCs) suffering from beneficial use impairments that remain under management through their AOC-specific remedial action plans (RAP). Contaminated sediments continue to be a major issue for most of the active AOCs due to direct and in-direct cause-effect linkages between sediment contamination and beneficial use impairments that include, among others, restrictions on fish and wildlife consumption, degradation of benthos, fish tumors and deformities and bird or animal deformities/reproductive problems (Szalinska et al., 2007; US EPA, 2013a, 2013b).

The Huron-Erie Corridor (HEC) is an international waterway linking the upper Great Lakes via Lake Huron to Lake Erie. It consists of two connecting channels, the St. Clair River and Detroit River coupled via the shallow Lake St. Clair (Figure 2.1). Both the St Clair and Detroit Rivers are designated as international Great Lakes AOCs (IJC, 1987)

and have associated remedial action plans (RAPs) tasked with implementing clean-up actions to address beneficial use impairments. Given that the Huron-Erie corridor runs through diverse agricultural, urbanized as well as highly industrialized regions, its two AOCs and Lake St. Clair receive pollution inputs from a complex array of point, non-point, small tributary and upstream sources (Szalinska et al., 2006). Contaminant sources are further complicated by inputs arising from additional AOCs, the Clinton and Rouge Rivers, which drain into the HEC. Beyond spatial complexity of pollution inputs, the HEC exhibits considerable hydraulic complexity that alters the distribution, transport and fate of contaminated particles (Szalinska et al., 2011). Dredged navigation channels running through the entire corridor provide substantive depth and flow relief compared to non-channelized waters, acting as hydraulic and thermal barriers to water parcel and particle mixing between adjacent U.S. and Canadian nearshore zones (Anderson et al., 2010). While the St. Clair River only has two islands in its main upper channel, it discharges to Lake St. Clair through a delta that includes several channels and an interior delta-lake. The Detroit River has several small and large islands in its upstream and downstream reaches leading to a high degree of channelization in conjunction with the major shipping channels (Coordinating Commitee on Great Lakes Basic Hydraulic and Hydrologic Data, 1998). The combined complexity of spatial distribution of pollution sources coupled with hydraulic complexity necessitates careful consideration of sampling design and subsequent approach to the geospatial interpretation of sediment contamination.

Technological advances in computing and database management along with the growing use of Geographic Information Systems (GIS) for spatial analysis have changed the way we map, design and evaluate the distribution of environmental attributes, making analysis of large-scale datasets easier and more manageable. Despite widespread availability and ease of use for off-the-shelf methods of spatial interpolation and contour mapping, such as kriging, such methods come with sets of assumptions that can produce misleading relationships unless properly defined through intensive preliminary statistical analysis of the data (Mueller et al., 2004). For example, most spatial interpolation and contour mapping methods are best applied to datasets with well-designed spatial structure, equally dispersed sampling designs with a high intensity of sampling, conditions of limited or randomized/multi-directional flow (high sample point connectivity), homogenous substrate type and limited bathymetric/elevation variation (Mueller et al., 2004). They are expected to perform less well in systems such as the HEC characterized by directional water flow, channelization related to hydraulic and/or island barriers or in meandering channels/steep river bends that distort connected sampling point proximities relative to their geospatial proximities in an assumed 2-dimensional homogenous plane. Many geospatial sampling designs applied to contaminated sediments also favor randomized sampling strategies rather than gridded sampling designs in order to comply with statistical assumptions when comparing pre-defined regions within the sampling area or to generate mass balance inventories of contaminated sediments (Drouillard et al., 2006; Szalinska et al., 2013).

Alternatives to spatial interpolation methods include local statistic approaches such as the Getis-Ord Gi* statistic that can be used to identify contaminated regions, i.e. contaminant 'hotspots', or areas that are unusual in their reduced level of contamination (contaminant 'cold spots'). The Getis-Ord Gi* statistic evaluates each sample site with its neighbors generating a new neighbor influenced mean concentration that is compared to the system wide mean and distribution of concentration values measured in the system (ESRI, 2016a). Clusters of sampling points in proximity to one another, and which exhibit reassigned concentrations that are significantly higher than the system-wide mean are identified as 'hot spots' whereas those significantly lower than the mean are characterized as 'cold spots'. Such an approach can avoid some of the pitfalls related to interpolation if additional information is utilized, i.e. consideration of barriers and known flow-discontinuities, when grouping sample clusters. Farah et al., 2012 was the first to apply the Getis-Ord statistic to environmental contaminants to identify ^{222}Rn contaminated wells used for drinking water in the state of Maine, USA. Szalinska et al. (2013) provided the first application of Getis-Ord to identify hot and cold zones of contaminated sediments (zinc, cadmium and polychlorinated biphenyls (PCBs)) in the Detroit River. However, similar to interpolation, the algorithm used to estimate neighbor influenced mean concentrations can bias interpretation if non-connected sampling points are grouped together in the revised neighbor influenced mean calculation. Getis-Ord is typically estimated in automated fashion using off-the-shelf GIS-tools that apply fixed distance (e.g. (Szalinska et al., 2013) or inverse distance algorithms (see methods). However, the estimation approach can

also be modified to apply a user-configured matrix where neighbor assignment weightings are manually altered.

The objective of this study was to compare three Getis-Ord approaches (fixed distance, inverse distance weighting and a user defined matrix that considers hydraulic and island barriers) to describe mercury contamination in sediments of the Huron-Erie corridor. Each approach was validated by comparison with a validation data set (20% of the total data randomly selected and reserved from use in hot and cold zone delineation). Furthermore, the robustness of the technique and sensitivity to the available sampling intensity for the HEC was examined by comparing hot and cold zone delineated areas across 5 different validation datasets randomly removed from the total. From the above contrasts, it is hypothesized that the user defined matrix will provide the most accurate map of total Hg hot zones and cold zones relative to the validation data set. Furthermore, it is expected that hot and cold zone areas will show little difference between maps generated with sub-sets of training datasets provided that the sampling design instituted had sufficient sample dispersion and sampling intensity.

2.2 – Methods

2.2.1 - Study Area

The Huron Erie Corridor (HEC) (Figure 2.1) is 157 km in length, with the St. Clair River being 65km long and receiving urban and industrial inputs on its upper Canadian shoreline from the city of Sarnia. Dropping 1.5m, the St. Clair River has an average flow

of 5200 m^3s^{-1} and is generally a single deep channel with depths from 8-15m except where obstructed by Stag and Fawn Island, leaving only a few depositional spots before it reaches the St. Clair Delta (Coordinating Commitee on Great Lakes Basic Hydraulic and Hydrologic Data, 1998). Upon reaching the St. Clair Delta, the flow decreases and the river splits into an expanse of meandering channels averaging 11m in depth and shallow bays creating a depositional zone and complex shoreline of islands covering 80km^2 (Szalinska et al., 2007). The eastern side of the delta (Chenal Ecarte, Johnston Channel) are more narrow, shallow waterways carrying lower water volumes. The Western side of the delta (North, Middle and South Channels) account for most volume to Lake St. Clair (Thomas et al., 2006). Lake St. Clair has a mean depth of 3.7m and is bisected by the 8.3m shipping channel from the southwest to the northeast (Forsythe et al., 2016). The lake is essentially divided by the channels cold water plume which prevents cross mixing as water moves to the Detroit River. The Detroit River has an average flow rate of 5240 m^3s^{-1} extending 51km and dropping 0.9m, starting on an east to west flow then bending to a north to south flow before it discharges into Lake Erie (Szalinska et al., 2013). The upper river mimics that of the St. Clair River being channelized and very narrow with two islands (Belle Isle and Peche Island) as its only obstructions. The lower river transforms into an abundance of large and small islands breaking the river into channels, bays and harbours with the average depth decreasing to as low as 3m except for the dredged navigational channels (Szalinska et al., 2013).

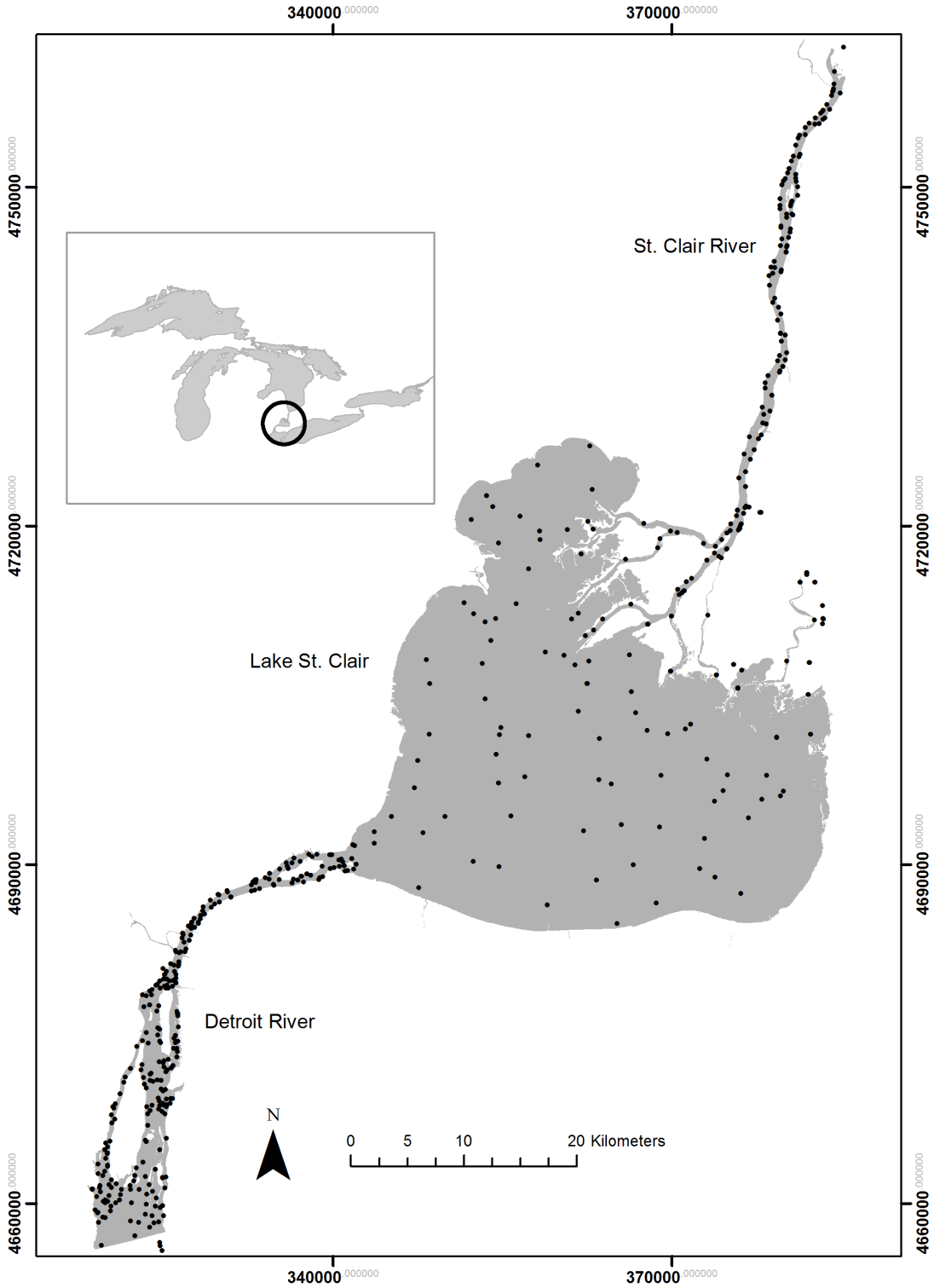

Figure 2.1 Study area, Location of sampling locations from all 6 surveys.

2.2.2 - Sample Collection and Laboratory Analysis

Data were collected from 6 separate surveys completed throughout the HEC over the last 18 years by the Great Lakes Institute for Environmental Research all following the same stratified random sampling protocol (Figure 2.1)**.** The surveys were completed as follows: 1999 and 2008/09 Detroit River surveys (river-wide surveys with n=150 and n=65 sampling points), 2004 full corridor (emphasizing St. Clair River and Lake St. Clair n=108), 2005 and 2012 Walpole Delta (n=38, n=48), and the 2013/2014 full corridor survey (n=223 sampling points). Individual sampling protocols and laboratory techniques have been described elsewhere (Szalinska et al., 2013, 2007, 2006). The stratified random sampling design used in each survey segmented the river and/or corridor into upstream-downstream reaches as well as U.S and Canadian waters. Coordinates for sampling were randomly pre-assigned throughout each segment with equal numbers of sample stations allocated in U.S. and Canadian waters but unequal sample numbers used among individual river/lake reaches. The only deviation from this sampling design was the sampling locations for the Walpole channels, which were triplicate samples, and taken at the same location in both 2005 and 2012. Sampling stations were accessed by boat and moored within 150 m of the pre-selected sample location. Surface sediment samples were collected using a petite ponar grab sampler (6 x 6”). Multiple sediment grabs were performed until a total volume of 2L of sediment was collected at the sample site. Duplicate samples (two 2L volumes) were collected at every fifth site to ensure compatibility. Where sufficient sediment could not be collected, the boat was moved by approximately 200 m and a new sample was

attempted for collection with the revised location coordinates noted. Following collection, samples were manually mixed and stored in plastic bags at 4°C until processing. At processing, all samples were sieved to ensure a grain size of <2 mm from which a subsample was taken for total Hg analysis.

Total Hg concentrations for the 1999, 2004, and 2005 surveys were measured by atomic absorption spectrophotometer (AAS-300, Varian) equipped with a single element hollow cathode lamp and a vapor generation accessory unit (VGA-76, Varian as described in (Szalinska et al., 2006). Total Hg for the 2008/09, 2012 and 2013/14 surveys was measured using a DMA-80 Direct Mercury Analyzer (ATS Scientific INC., Burlington, ON). Despite differences in the method for total Hg between surveys, common sediment reference materials (NRCC MES-3, LSKD-4) and in-house references were analyzed with each sample batch of 30, along with both replicate and duplicate samples ensuring method compatibility. The Canadian Analytical Laboratories Association (CALA) standard operating procedures were conformed to for all laboratory methods.

2.2.3 - Data Analysis

Szalinska et al. (2013) demonstrated no significant changes in Hg concentrations in sediments of the Detroit River over the 1998-2008/09 period. A formal assessment of temporal changes in Hg and other contaminants from sediments of the Huron-Erie corridor is the topic for a separate study (Chapter 3 of this thesis). The main objective of the present research was to compare and contrast different hot and cold zone delineation techniques which requires robust sample resolution and dispersion.

Therefore, data from individual surveys were combined into a single database to bolster sampling intensity. This assumes that temporal trends in Hg concentrations are small or negligible compared to spatial gradients present within the system. All data was tested for normality using Shapiro-Wilk's test and log normalized before analysis. The combined database was further divided into a training and validation data set. The training data set consisted of 80% of the database sites selected by randomization procedure. The remaining sample sites were assigned as validation data. The 80% allocation for the training dataset was selected following various interval testing and was found to be the optimal interval at both allowing sufficient data for creation of interpolation maps but also to provide sufficient samples for validation.

The Hot Spot Analysis tool (ESRI, 2016a) was utilized to calculate the Getis-Ord Gi* statistic for each sample site in the training data set. The Gi* statistic generates a new local mean Hg concentration for each site based on its measured value as well as Hg concentrations measured at neighboring sites within a user defined threshold distance. The new neighbor influenced mean concentration is then compared against the system wide mean and distribution of mercury concentrations in the training data set to assign its category as a hot spot, cold spot or of intermediate concentration. When the neighbor influenced mean concentration falls within a user defined distribution interval of the system wide mean it is designated as intermediate. When it exceeds the specified distribution interval it is assigned as a hot spot and when it is lower than the interval it is assigned as a cold spot. So if the concentration of a given contaminant, mercury in this case, is above the threshold of its distribution values it will

be referred to as a hot spot. For purposes of the present analysis, a distribution interval of 90% (90^{th} percentile) was utilized corresponding to a probability of significant difference from the corridor wide mean of less than 0.10. A threshold distance of 5000m was set in all three methods to ensure each sampling location had multiple neighbors and to provide consistency in neighbor selection across the methods.

The three methods for Getis-Ord Gi* (Fixed Distance, Inverse Distance and User defined Matrix) each differ in how the local mean concentration is calculated. Two of the methods are available as automated tools in ArcGIS and were applied as is to the training data set (ESRI, 2016b). They were accessed within the Hot Spot Analysis tool of ArcGIS using the Conceptualization of Spatial Relationships parameter option (ESRI, 2016b). The Fixed Distance method is the default spatial relationship used by the Hot Spot Analysis tool and was previously used to identify hot and cold spots in the Detroit River (Szalinska et al., 2013). In this method, all neighbors within the specified distance threshold (5000 m) are assigned equal weights to calculate the local mean concentration. Sample sites that fall outside of the distance threshold are excluded from the local mean concentration calculation. The Inverse Distance method is performed by selection of the Inverse Distance band from the Conceptualization of Spatial Relationships parameter of the Hot Spot Analysis tool. This imposes a distance decay algorithm using a logarithmic curve that assigns different weights to each neighboring station based on its proximity to the station in question. Thus, neighbor sampling sites in close proximity to the station are assigned higher weights compared to those located further away giving them a higher influence on the local mean

concentration estimate. As in the case for the fixed distance method, only neighbor sites falling within the threshold distance of 5000 m are included in the new local mean concentration estimate, all others have an effective weight of zero.

The User defined Matrix method is a modification of the fixed distance approach. Similar to the fixed distance, neighbors within the threshold distance are given equal weights when calculating the local mean concentration. However, some neighbors are censored from the local mean concentration calculation based on their lack of physical connectivity to the local site even though they fall within the distance threshold criteria. In this case, data on bathymetry, directionality of water flow and island barriers were used to censor neighbors considered not hydraulically connected to a given site. This was established by overlaying sample locations against external map layers consisting of depth charts, a hydraulic flow map (Anderson et al., 2010, 2014 dataset) and island locations. Within the ArcGIS software, the Get Spatial Weights from File (User defined Matrix Method) option was selected. The original fixed distance matrix was used as the initial input and then manually adjusted by assigning neighbors to be censored a weight of 0 in the matrix. Three rules were used to identify which neighbors were censored: i) neighbors that were on the opposite side of islands or land barriers; ii) neighbors that were found on the opposite side of navigation channels and iii) neighbors that were downstream of the station relative to the direction of water flow.

After performing the Getis-Ord analysis according to the thee methods, a coarse interpolation was used to establish polygon areas consisting of hot, cold or intermediate

zones throughout the HEC. Initially, polygons joining clusters of sample locations with similar Getis-Ord category assignments were drawn. However, an automated approach was considered more desirable. To facilitate this, a 250 x 250m grid was assigned over the entire HEC. Each cell in the grid was assigned to the 3 categories (hot, cold or intermediate) based on its nearest sample location assignment from Hot Spot Analysis using the Spatial Join tool. Common cells were then merged together using the Dissolve tool. Over several exploratory trials it was observed that the automated approach and manual polygon approach yielded similar maps with respect to the location and general size of hot and cold zone polygons. Thus, the automated approach was selected to provide a consistent interpolation across the three Getis-Ord methods and between individual trials. Hot zone and cold zone areas on a per zone basis were computed by summing the number of cells and their corresponding areas contained within each polygon region where there were at least 3 cells with a common categorization. Total hot and cold zone areas were measured by summing all cells and their areas with the corresponding categorization by waterbody and throughout the system.

The robustness of the interpolation maps across training set trials was evaluated in order to provide a sensitivity analysis to sample station dispersion given a fixed sampling resolution (n=131 for a given training data set). Two metrics were used as part of the sensitivity analysis. First, the mean, standard deviation and coefficient of variation of total area of hot and cold zones was completed for each of the three methods based on data from across the trials. Second, a qualitative evaluation of the location of major hot and cold zone polygons was examined by comparing the five

interpolation maps generated by each data set and method to look for discrepancies in the location of major polygons by technique.

To validate each Getis-Ord method, the validation dataset was contrasted against the interpolation map generated by the training dataset. When a validation sample point was within the 90% distribution interval of the system wide mean and its corresponding grid cell of the interpolation map was given as intermediate, the assignment was considered correct. Similarly, when the validation site concentration was outside of the distribution interval and it matched either a hot or cold zone assignment for the same cell in the interpolation map, the assignment was considered correct. Wrong assignments were assigned when the validation data point fell within a different concentration interval than the associated cell assignment for the interpolation map. However, despite having over 130 sample points in the validation data set, it was observed that most validation data points fell within the intermediate zone and it was somewhat rare that validation points fell into the smaller polygon areas designated as hot and cold zones. This made distinguishing between the 3 Getis-Ord approaches difficult when applied to a single training/validation data set combination. To reduce this issue, we generated 5 different training and associated validation data sets using separate randomization procedures to generate each data set (designated herein as a trial). Each trial was then validated with its corresponding validation data set. The cumulative correct and incorrect assignments by each category were then generated across the 5 trials similar in principle to a jackknifing approach and used in method validation. Following selection of the most accurate method according to

validation, a finalized interpolation map was generated using 100% of the Hg dataset in order to present the most complete map of Hg distribution in the HEC and for each of the respective waterbodies.

2.3 - Results

Each training dataset included n=522 sites (80%) and each validation dataset included n=131 sites (20%). The global geomean (inclusive of training and validation data) was 0.13 (0.11-0.14) ug g^{-1} total Hg and 0.13 (0.11-0.14) ug g^{-1} in the first training dataset. There were no significant differences in the corridor wide geomean Hg concentration estimates across the five training datasets relative to one another or to the global mean. Mercury concentrations at 55 sites (8%) of the full data set were greater than the 90% sampling interval with the highest total Hg concentration value equal to 9.14 ug g^{-1}. Of these, 23 sites exceeded the Probable Effect Concentration (PEC) consensus based sediment quality guideline of 1.06 ug g^{-1} (MacDonald et al., 2000). The general locations of high contamination sites within the HEC corresponded to Canadian portions of the midstream St. Clair river, Walpole Island channels, midstream Detroit River, and southern U.S. portion of the Detroit River including Trenton Channel. Mercury concentrations at 82 sites (12%) were below the 90% sampling distribution interval. These low value groupings were generally located on the U.S. side of the St. Clair River and Lake St. Clair and at localized areas below the midstream of the Detroit river. Mercury was not correlated with environmental variables such as TOC, bottom water velocity or grain size distribution.

Table 2.1 provides the results of sensitivity analysis based on total area of hot, cold and intermediate zones across the 3 Getis-Ord techniques and between each trial. The fixed distance method generated the largest total hot and cold zone areas throughout the corridor followed by the user defined matrix approach. The inverse distance generated the smallest hot and cold zone polygons with 93% of the total area of the HEC being designated as intermediate. Differences in the relative sizes of hot versus cold zones were evident among the techniques. The fixed distance and user defined matrix methods were more consistent to one another in the overall area of cold zone polygon areas whereas for the hot zone areas the user defined matrix and inverse distance more closely resembled one another. These differences in cumulative categorical sizes were generally robust across individual trials. The intermediate area had the lowest coefficient of variations (CV) across trials ranging from 2.3 to 5.5% between methods. This was expected because most samples fall within this category and therefore random removal/replacement of 20% of the data between trials has little impact on the number of samples that fall into the intermediate category. For the cumulative hot zone area, the inverse distance generated the lowest CV (9.1%) across trials, while the fixed distance and user defined matrix approach were more comparable to one another (CV's of 19.3 and 21.3%, respectively). Similarly, CVs for the cold zone areas by fixed distance and user defined matrix were comparable to one another and of similar magnitude to their hot zone counterparts. In contrast, the inverse distance showed a very high CV (51%) for the cumulative cold zone area indicating higher sensitivity for the category to sample dispersion artifacts.

Table 2.1 Total area for each method expressed as percent of total. Mean and Standard deviation expressed for 5 subsets.

	Trial 1	Trial 2	Trail 3	Trial 4	Trial 5	Mean	Std Dev	CV (%)
Fixed Distance								
Sum Hot zone Area %	13.8	10.4	17.9	14.4	13.4	**14.0**	2.7	19.3
Sum Cold zone Area %	20.4	23.9	15.2	17.3	22.4	**19.8**	3.5	17.7
Sum Intermediate Area %	65.9	65.7	66.8	68.3	64.2	**66.2**	1.5	2.3
Inverse Distance								
Sum Hot zone Area %	2.3	2.2	2.3	2.5	1.9	**2.2**	0.2	9.1
Sum Cold zone Area %	3.9	7.8	1.9	3.7	7.2	**4.9**	2.5	51.0
Sum Intermediate Area %	93.9	90.1	95.8	93.8	90.8	**92.9**	2.4	2.6
User Specified Matrix								
Sum Hot zone Area %	3.8	4.6	6.4	4.4	4.5	**4.7**	1.0	21.3
Sum Cold zone Area %	17.2	22.7	16.5	12.8	22.5	**18.3**	4.2	22.9
Sum Intermediate Area %	78.9	72.7	77.2	82.8	73.0	**76.9**	4.2	5.5

A comparison of interpolation maps created on one randomly selected trial (Trial 2) using the three methods is provided in Figure 2.2. In accordance with the data from Table 2.1, the fixed distance method produced larger hot and cold zones throughout the corridor. Hot zones generated using this approach included much of the delta channels, a very large central zone in Lake St. Clair, a small zone in the midstream portion of the Detroit River and the entire U.S. portion of the downstream Detroit River below the midpoint of Grosse Isle. Cold zones encompass binational waters of the upper portion and mid-section of St. Clair River, much of the northern U.S. section of Lake St. Clair and the Lake St. Clair/upper Detroit River confluence region. No hot zones were identified by the fixed distance method in the St. Clair river which differs from the other two approaches.

Hot zones by inverse distance approach were identified in portions of the Canadian waters of the upper St. Clair River, portions of the Delta and their receiving waters of Lake St. Clair and in the upper and lower U.S. waters of the Detroit River. Cold zones by the inverse distance method were similar in location to major cold zones produced by the fixed distance but of much smaller area.

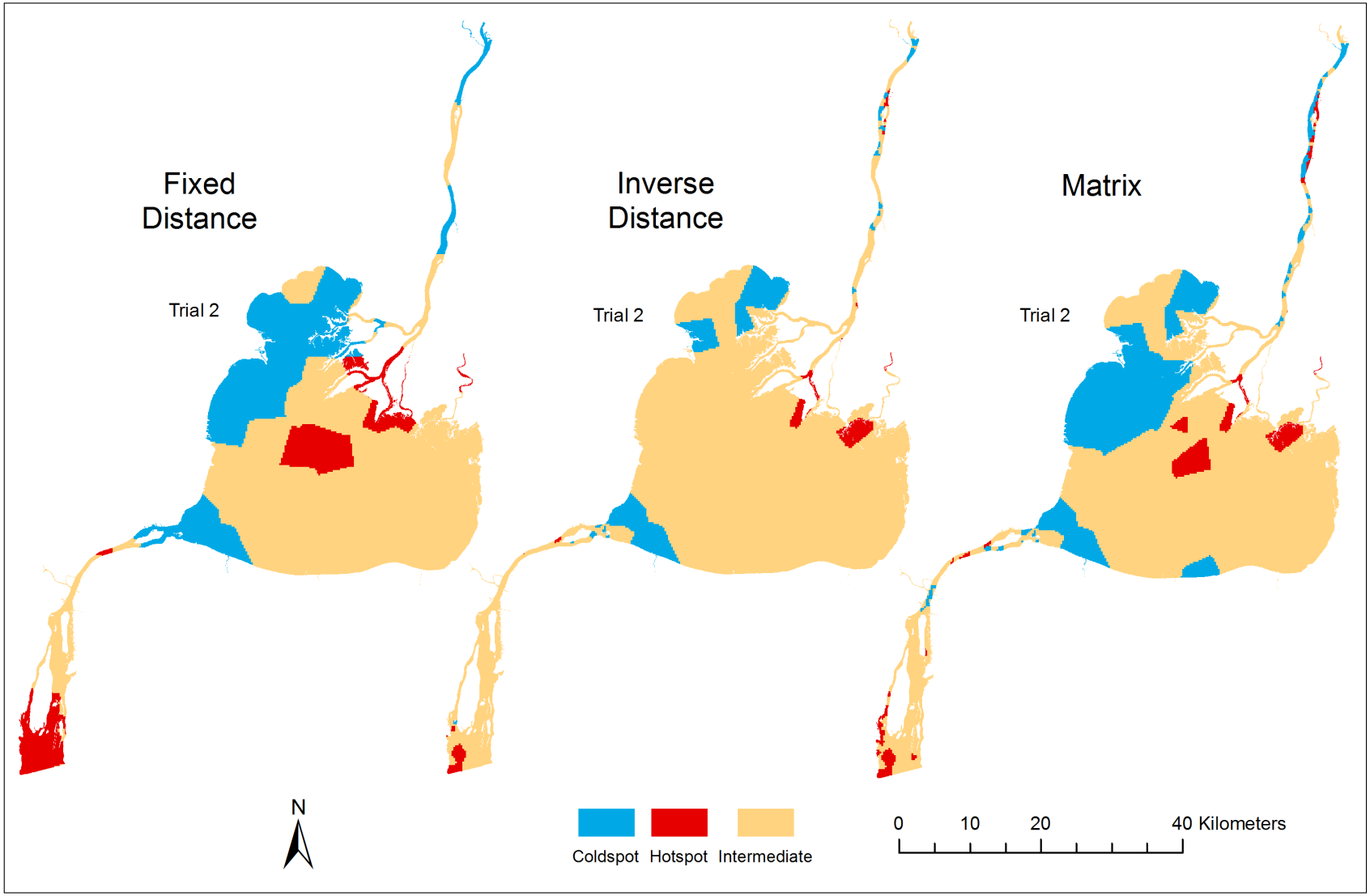

Figure 2.2 Map Comparison of Hot and Cold Zones generated for Trial 2. Red, blue and beige designate hot, cold and intermediate zones.

The user defined matrix method produces a map that was intermediate between that of the fixed and inverse distance methods. Hot zones in the upper St. Clair river were the most extensive when generated by the user defined approach and extended above and below Stag island in Canadian nearshore waters. The delta hot zones bore strong resemblance to that of the inverse distance map while the large central Lake St. Clair hot zone identified by the fixed distance is broken into two smaller areas but in the same general location for the user defined matrix. For the Detroit River, nearshore U.S. hot zones occur in the upper U.S. waters, a small binational hot zone in the middle reach and in an extended zone in the lower U.S. portion of the Detroit River that includes approximately half of the Trenton Channel. Cold zones by the user defined matrix were generally similar for Lake St. Clair with the other methods with the exception of a new cold zone being uniquely identified in Southern Canadian waters. The matrix approach also distinguished itself by generating cold zones over much larger U.S. portions of the St. Clair River and as a series of localized cold zones in the Detroit River.

Variance in the hot and cold zone locations for a given method across individual trials was considered relatively small. Appendix 1- Appendix 3 provides individual trial interpolation maps for each method while Appendix 4 showcases each method inclusive of all sample points. Based on location, fixed distance maps show virtually no change with respect to boundaries of hot zones in the Trenton Channel and Walpole delta along with cold zones in the St. Clair River and upstream Detroit River. Variability was more apparent in Lake St. Clair where connectivity of separate hot zones and cold zones was

variable across trials, sometimes regions were linked together into one larger zone and other times they were separated.

The inverse distance method generally identified similar hot and cold zone boundaries in upper St Clair River, along with small hot zones in the Walpole Delta across trials. There was common identification of cold zones in the upstream Detroit River though variability in the large Canadian cold zone was found in 2 out of 5 trials. A similar pattern was observed in the upper U.S. side of Lake St. Clair. Greater variation across trials with the inverse distance method was apparent in the hot zone within Trenton Channel.

The user specific matrix showed small variability in respective hot and cold zones across trials. Both hot and cold zones boundaries were similar between trials for the St. Clair river and Walpole delta. Hot zones and cold zones in Lake St. Clair commonly encompassed a large general zone of the U.S. portion of upper of the lake, while hotspots were located in the center of the lake in Canadian waters. These similar patterns were observed between trials though linkages and exact boundaries varied across trials. Within the Detroit River, commonly identified hot zones across trials were in the Trenton channel and midstream section while cold zones in the upstream and lower midstream section remained consistent across trials. Overall, the sensitivity analysis showed that each method was relatively robust in terms of the interpolation maps generated across individual trials and produced generally similar polygon sizes and locations for hot and cold zones. The only exception appeared to be a high degree of

variability between trials in the delineation of cold zone polygons by the inverse distance map (See Table 2.1 and Appendix 2).

Table 2.2 presents the method validation results for individual training dataset trials as well summary statistics across trials. On the basis of total percent correct predictions, the inverse distance method generated the highest accuracy (79%) closely followed by the user defined matrix (74%) while the lowest accuracy occurred for the fixed distance (57%) approach. Kruskal-Wallis multiple comparison tests indicated that the inverse distance method had significantly higher ($p<0.01$) accuracy compared to the fixed distance approach, but there were no significant differences in the accuracy between the user defined matrix approach and inverse distance. Table 2.2 also provides a breakdown of model accuracy within the hot and cold zones respectively. For these comparisons, the number of validation stations falling in hot or cold zone polygons were lower relative to intermediate zones and varied between individual trials due to the randomization procedure used for data selection. Correct assignments for hot zones were lower but mirrored the total % correct assignment patterns ranging from 14 to 34% across methods. Kruskal-Wallis multiple comparison indicated a similar pattern of accuracy for hot zones as identified by the total correct assignments. For the cold zones, a different pattern emerged. The highest correct assignment was observed for user defined approach (37%). However, Kruskal-Wallis multiple comparison tests could not discriminate between the cold zone accuracy across methods. In the majority of cases, the incorrect assignments for validation data occurred under the condition where the observed concentration was within one category of difference than the predicted

concentration interval. In other words, it was rare that a given validation station for example having a mercury concentration equal to a cold zone concentration was located in a hot zone polygon or vice versa. For hot zone mis-categorizations of this extreme type, the mean± standard deviation percentage of incorrect assignments was 2.2±2.1, 2.9±6.4 and 2.0±4.5% for the fixed, inverse distance and user defined matrix approaches, respectively. For cold zones it was 0.9±1.9, 0 and 0% for the fixed, inverse distance and user defined matrix methods.

Table 2.2 Validation expected vs observed results.

% Correct Assignments	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Mean±SD
Total Correct Predictions						
Fixed Distance	65.6	55.7	51.9	59.5	51.9	56.9±5.8[1]
Inverse Distance	80.9	80.9	77.9	77.9	75.6	78.6±2.3[2]
User Specified Matrix	75.6	76.3	69.5	74.0	72.5	73.6±2.7[1,2]
Correct Hot Zone Predictions						
Fixed Distance	15.8	18.5	12.1	15.6	8.7	14.1±3.8[1]
Inverse Distance	28.6	45.5	20.0	30.8	44.4	33.9±10.9[2]
User Specified Matrix	20.0	36.4	16.7	25.0	26.7	25.0±7.5[1,2]
Correct Cold Zone Predictions						
Fixed Distance	22.7	20.0	21.7	50.0	25.7	28.0±12.5[1]
Inverse Distance	20	36.4	60.0	0	25.0	28.3±22.1[1]
User Specified Matrix	34.8	33.3	26.3	44.4	44.4	36.6±7.8[1]

2.4 - Discussion

The evaluation of the three Getis-Ord statistic approaches demonstrated differences in spatial relationships and identification of localized hot and cold zones throughout the HEC. Sensitivity analysis was evaluated by two metrics to understand if the sampling density was sufficient within the corridor to identify hot and cold zones. Overall, each method was found to be relatively robust when compared across individual trials that re-randomized the selection of sample stations used for each trial training data set. This suggests that a sampling density of 500 + sampling stations in the HEC was adequate for describing general spatial patterns of Hg in this system. However, the sampling resolution required will vary for different systems and contaminants depending on the degree of heterogeneity of spatial patterns present arising from various environmental factors that govern the distribution and fate of the contaminant of interest and complexity of sources (number of sources and their locations) for the pollutant. The highest CV for trial sensitivity was observed for the inverse distance cold zone total area while the lowest CV was for the inverse distance hot zone area. This method is the most strongly influenced by individual sample locations, especially those without close neighbors given the distance decay algorithm used in local mean calculation for this technique. The fixed distance method and user defined matrix approaches were more comparable to one another with respect to their sensitivity across trials. Most of the change was observed in zone boundaries between trials for Lake St. Clair where distance between sampling stations was at its greatest.

The trial validations indicated higher accuracy of two of the three Getis-Ord approaches, inverse distance and user defined matrix, which generated between 70 – 81% total correct categorical assignments of the validation data. It is not surprising that the inverse distance had a slight advantage in its model accuracy because it produced the smallest areas for hot and cold zones, respectively. Thus, when validation data fell within an identified hot or cold zone generated by the technique, it fell in close proximity to one of the training sampling stations with equivalent local mean categories. There were also fewer validation stations that fell into hot and cold zones identified by the inverse distance method compared to the other techniques which accounts for the higher variability in validation results across trials. Unfortunately, the method of reserving a randomly selected validation set for trials resulted in low numbers of validation stations falling within the regions of interest (hot or cold zones). A much stronger approach to validation would be to apply an independent sampling survey directed by the different Getis-Ord maps identified in Figure 2.2 to specifically test hot and cold zone boundary differences between the methods. This was outside of the scope of the current research capacity.

The maps generated using the inverse distance and fixed distance approaches, particularly within the AOCs, also had stronger correspondence to spatial patterns previously identified for these rivers in the literature. For the St. Clair River, both the inverse distance and user defined matrix identified a significant hot zone isolated in Canadian waters in the vicinity of Stag Island that was not identified by the fixed distance approach. This region was historically identified as a known contamination

zone from Sarnia's chemical valley and historical chlori-alkali facilities being identified as early as the 1970's by (Thomas, 1974). This area was further confirmed by (Mudroch and Hill, 1989) and (Marvin et al., 2004). Though these studies can date back close to 50 years and confirmed decreases in Hg concentrations were observed over time by 2004 from (Szalinska et al., 2007). The same distributional patterns are continually found in the zone of mitigation that is still apparent in its elevated mercury concentrations to the present day. A more recent contrast by (Richman and Milani, 2010) from samples taken in 2006 and 2008 still confirmed that Hg is found elevated in these regions though concentrations have begun to show little change in recent years. This area historically identified corresponds the closest with the User defined matrix method but more importantly identifies that the fixed distance method failed to locate a known historical region of high contamination.

For the Detroit River, the lower river hot zone identified by the fixed distance method included both the U.S. and Canadian boundaries which is not consistent with the literature. The Trenton channel area of the downstream U.S. side of the Detroit River has been identified as a significantly contaminated zone found to be one of the primary sources of contaminants to Lake Erie (Besser et al., 1996; Hamdy and Post, 1985; Painter et al., 2001). Comparison of reference sites found on fighting island showed the U.S. side Trenton Channel had significantly higher concentrations of contaminants in sediments, including Hg (Besser et al., 1996), which were consistent with the analysis done by (Szalinska et al., 2006) comparing the Canadian and U.S. downstream sites. This demonstrates that the Fixed distance method may overestimate

the size of the hot zone. Addtionally, the Trenton channel pattern of contamination observed in previous studies and reports indicating contamination from upper Trenton channel all the way throughout the southern tip of Grosse Ile (US EPA, 2010) is also more compatible in the user defined matrix then in comparison to the inverse distance method. The historical remediation areas found within the Trenton channel extend from the top of Grosse Ile all the way down to the end including zones such as the BASF Riverview Property, Black Lagoon, and Elizabeth Park Marina (Besser et al., 1996; Drouillard et al., 2006; Hartig et al., 2004; Szalinska et al., 2006) encompass the specific area that the User defined matrix encompasses while the Inverse distance method only identifies a hot zone beyond the southern end of Grosse Ile. Furthermore, upstream Detroit River hotzones identified in the User defined matrix also corresponds with the Carter industrial Site and the Conners Creek areas of contamination previously targeted for remediation (Hartig et al., 2004).

For Lake St. Clair, there was a variance in observations of hot and cold zones between the three methods. Historically, independent studies dating back (Mudroch and Hill, 1989; Thomas, 1974) had identified the highest Hg concentrations in the central and east-central areas in the center of the lake. These early identified patterns were continually identified into the 2000's by Marvin et al., 2004 and Gewurtz et al., 2007 for elevated concentrations focused on the Canadian side in the center, deepest portions of the lake. An additional trend noted was that the Upper U.S. side of the lake was found to have the lowest concentrations throughout the waterbody. In corroboration to each method, both the fixed-distance and user defined matrix

methods identified a large hot zone in the center of the lake whilst the inverse distance failed to identify any. Similarly, for cold zone regions both the fixed distance and user defined matrix corresponded well with other studies identifying a large cold region on the upper U.S. side of the lake, which the inverse distance only identified on a very small scale with two localized cold spots. We should note that the variance of the fixed distances approach across trials tended to be lower for fixed distance in the Lake compared to the AOCs. In comparison to a different geo-statistical mapping technique, Forsythe et al. (2016) performed an independent assessment of mercury in Lake St. Clair. In the above study the authors applied a grid sampling approach encompassing the entire lake. They then used a geovisualization interpolation technique that considered both bathymetry and measured contaminant concentrations. Their study implicated an enriched mercury hot zone near the center of the lake consistent with the central zone identified in the present research by the fixed distance and matrix approach, as well as the historical findings, indicative that different geo-statistical mapping techniques resulted in the same findings across approaches.

Limitations of the fixed distance approach, particularly as it applies to the AOCs, occur due to their riverine characteristics in which the length far exceeds the width. This coupled with substantive depth relief associated with shipping channels and strong directional water flow decreases cross channel mixing causing adjacent nearshore areas to become isolated from one another. As such, Canadian point sources are carried downstream by sediment resuspension events but are less likely to be carried across to U.S. waters and vice versa (Szalinska et al., 2011). The fixed distance approach has no

mechanism to account for physical isolation of sampling stations within the distance threshold limit and as such either masks distinct nearshore differences across the channel, as was the case for St. Clair River, or over extends hot zones as was the case for the lower Detroit River. Interestingly, the inverse distance approach was apparently immune to these artifacts even though the technique also does not explicitly account for land or hydraulic barriers. This occurred because the dispersion of sampling points tended to favor nearshore areas within the AOCs which maximized the distance between sampling stations along adjacent shorelines and reduced their neighbor influence with one another. Although this was unintentional as part of the original randomized sampling designs, the frequent failure to recover sediments using a ponar grab sampler within the rapid flowing and highly scoured bottom of shipping channels commonly caused relocation of 'alternate' sampling stations towards the closest nearshore area. However, if sample dispersion was more even across the channels, the inverse distance may be subject to zone boundary artifacts particularly in sections where the channel is narrowest in its cross section. The user defined matrix was developed specifically to account for hydraulic barriers and yielded hot and cold zone patterns in the AOCs that were similar, but extended in overall area over the inverse distance approach.

For the lake, the three methods produced more comparable maps with generally similar centroid positions of major hot and cold zone locations that varied in size between the techniques. This was expected because the lake is considered more homogenous and has a much smaller area of hydraulic barrier (a single shipping

channel) relative to the lake's surface area. However, sample station density in the lake was lower compared to the AOCs increasing the distance between neighbor stations. This resulted in the inverse distance approach becoming more fragmented compared to the other two approaches and heavily influenced by individual stations. As a result, the larger hot zone in the center of the lake was not identified by the inverse distance approach even though such a zone has been characterized independently in other studies (Forsythe et al., 2016; Gewurtz et al., 2007; Marvin et al., 2004). With the sampling distribution being more evenly dispersed and with no significant physical or hydraulic barriers in the lake, the fixed distance method was able to provide an accurate representation similar to that of the user defined matrix. Though failing to properly represent linear systems such as rivers, the fixed distance method may be more appropriately applied to large systems not constrained by tight boundary's and similar in magnitude in both a north-south and east-west direction.

Overall, the weight of evidence could not distinguish between the user defined and inverse distance approaches in terms of sensitivity and accuracy as applied to Hg patterns in the AOCs. However, the user defined matrix did identify a Hg hot zone in the lake center that was consistent with independent spatial patterns identified for Hg in the lake (Forsythe et al., 2016; Gewurtz et al., 2007) and as a result is considered the most appropriate corridor wide interpolation technique. The application of Getis-Ord to this unique and complex river system benefits by additional information concerning sample connectivity as implemented in the user defined matrix approach in this study. For river-systems with flow barriers and consistent flow directionality, spatial

connectivity between sampling stations is not merely a matter of two dimensional distance. In this study, we show that the different methods contribute to differences in the spatial inferences measured. We suspect that other aquatic systems, i.e. meandering streams with exaggerated bends may be even more biased depending on the interpolation approach applied using off the shelf GIS tools as applied here. The user defined matrix as outlined in the present study offers a simple means of accounting for hydraulic and land based barriers coupled with off the shelf tools without extensive requirement of programming or building dedicated hydraulic models. However, the creation of a user defined matrix requires more effort and additional information layers such as water velocities, direction of flow, bathymetry over off the shelf tools.

2.5 - Conclusion

This study aimed to compare and evaluate three Getis-Ord hotspot approaches; the previously implemented fixed distance approach, an inverse distance approach and a user defined matrix accounting for hydraulic and physical barriers in order to find the most appropriate method for identification of hot and cold zones in the Huron-Erie Corridor. Using mercury as a test parameter due to its anthropogenic nature and history within the corridor, the study revealed that the fixed distance approach was least accurate when used in this system. Based on validation statistics the inverse distance method was found to be slightly more accurate than the user defined matrix, however, the user defined matrix appeared to excel in its patterns identified for Lake St. Clair based on comparisons with literature identified spatial trends. As such, the user defined

matrix was concluded to be the most appropriate method for identification of hot and cold zones of Hg in the HEC. This method provides a simple modification to existing off the shelf software tools to incorporate realistic barriers between sampling stations that otherwise are not accounted for by fixed distance or inverse distance methods.

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CHAPTER 3 – PRIORITY CONTAMINANTS IN THE SEDIMENTS OF THE HURON-ERIE CORRIDOR: A COMPARISON OF SPATIAL AND TEMPORAL PATTERNS BETWEEN 1999 – 2014.

3.1 - Introduction

The Laurentian Great Lakes contain 18% of the world's surface freshwater yet are subject to a number of environmental stressors related to human population density, landscape changes and loadings of toxic pollutants (Grapentine, 2009; Szalinska et al., 2007). At present, the Great Lakes Water Quality Agreement (GLWQA) identifies 35 active (non-delisted) Areas of Concern (AOCs) due to assessed beneficial use impairments (BUI's) in each location. Both the Detroit River and the St. Clair River are identified as International AOC's and have Remedial Action Plans (RAPs) associated with them. The above connecting channels are hydraulically linked to one another by Lake St. Clair and together these three waterbodies comprise the Huron-Erie Corridor (HEC) linking the upper and lower Great Lakes.

Contaminated sediments are considered an important factor in the clean-up strategies of both the St. Clair and Detroit River RAPs due to their direct and in direct linkages to many, up to 11 of 14 BUI's, identified in each system (Szalinska et al., 2007; US EPA, 2013a, 2013b). Lake St. Clair was the first Great Lakes location to have its commercial fishery closed due to mercury (Hg) contamination of its fish in the early 1970's and continues to have elevated Hg within its sediments (Marvin et al., 2004a). Lake St. Clair and the St. Clair/Detroit Rivers have each been subject to extensive past surveys of contaminated sediments (Besser et al., 1996; Drouillard et al., 2006; Gewurtz et al., 2007; Hamdy and Post, 1985; Pugsley et al., 1985; Richman and Milani, 2010;

Szalinska et al., 2013, 2011, 2006). These studies have previously identified high contamination sub-regions including the mid-reach section of the St. Clair River downstream of the city of Sarnia, Ontario, Canada (Mudroch and Hill, 1989; Richman and Milani, 2010; Thomas, 1974), a large mass of mercury in the center of Lake St. Clair (Forsythe et al., 2016; Gewurtz et al., 2007; Marvin et al., 2004a) and multi-pollutant contamination of Trenton Channel of the Detroit River located downstream of the City of Detroit, Michigan, USA (Besser et al., 1996; Drouillard et al., 2006; Hamdy and Post, 1985; Pugsley et al., 1985; Szalinska et al., 2006). However, with the exception of a limited number of studies (e.g. Szalinska et al. 2007, 2011), most surveys conducted in the HEC have focused on only one of the connecting channels or lake making relative comparisons between systems difficult.

Past surveys of sediment contamination also differ with respect to the types of sampling design applied. The two main designs implemented in the HEC include a) Point source tracking (judgmental) and b) probability based sampling designs. Point source tracking designs designate sampling location based on previous information or expert knowledge concerning the location of point sources and known/anticipated depositional zones within the study system. Designs of this type are best suited for small sampling scales as they can maximize sample resolution and density in perceived priority locations. Designs of this type were applied within the Upper Great Lakes Connecting Channels studies (UGLCCS, 1988) and are commonly used to designate areas for clean-up or to monitor for local improvement following clean-up and mitigation activities (Zarull et al., 2001; Hartig et al., 2009; Thornley and Hamdy, 1984). However, surveys of

this type can provide a biased perspective of the overall system health especially when collated in weight of evidence assessments since regions of sampling are typically concentrated at known/perceived polluted locations. They can also misrepresent improvements through time in hydraulically active systems since a change in concentration at a given field station may be due to localized sediment redistribution during storm events, ice jams or other scour events rather than actual improvements in the overall sediment quality of the system. Probability based designs randomize sampling locations though out the study system, usually under a pre-designated stratified random sampling design. Probability based designs are more appropriate when applied at the entire system scale, enable unbiased statistical comparison of contamination between sampled strata, computation of regional and global mass balance inventories and can identify previously unknown contaminated and/or reference areas within the system (Szalinska et al. 2013). However, these designs can suffer from sampling resolution deficiencies depending on the scale of system being studied and degree of heterogeneity in sediment contamination patterns that occur (Szalinska et al. 2013).

The first large-scale probability based sediment survey in the HEC was implemented in 1999 in the Detroit River (Drouillard et al., 2006; Szalinska et al., 2006). This survey included 150 sampling stations that covered the entire AOC boundary, distributed samples equally in U.S. and Canadian waters and further stratified the AOC into upstream, midstream and downstream reaches. Priority contaminants analyzed including trace metals, total mercury (Hg), polychlorinated biphenyls (PCBs), polycyclic

aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCs) along with sediment characteristics such as grain size and loss on ignition. In 2004, a second probability based survey was generated for the Huron-Erie corridor that included 104 sampling stations distributed in St. Clair River, Lake St. Clair and Detroit River using similar sampling design attributes (Szalinska et al. 2007; Szalinska et al. 2010). Additional probability based surveys have been implemented in the Detroit River since 1999 (Szalinska et al. 2013) and the present study describes and combines the result of these past surveys with a new Huron-Erie corridor survey implemented in 2013-2014. Initial data interpretations of the above sediment surveys focused on regional comparisons of sediment quality (Drouillard et al., 2006; Szalinska et al., 2007, 2006). Szalinska et al. (2013) adopted mass balance approaches as well advanced GIS-techniques (Getis-Ord local statistic) to further evaluate local regions of highly contaminated and prospective reference areas containing background contamination levels for selected contaminants in the Detroit River.

The main objective of this study is to provide a spatial and temporal assessment of multi-pollutant sediment contamination of the Huron-Erie corridor applying regional, local and temporal assessment techniques previously implemented for the Detroit River. Data from previous probability based sediment surveys conducted in the HEC were compiled and collated along with the most recent survey (2013-2014) into a single georeferenced database. Temporal changes in sediment quality were compared over data compiled in the early year period (1999-2005) versus the late period (2008-2014). Spatial patterns were delineated at the system scale, waterbody scale, U.S. versus

Canadian jurisdictions and at local scales using a modified Getis-Ord method as described in Chapter 2. In addition to concentration changes, priority pollutant inventories were generated for each waterbody using a mass balance approach.

3.2 - Methods

3.2.1 - Study Area

The Huron Erie Corridor (HEC) is a 157 km waterway linking Lake Huron to Lake Erie. The St. Clair River is 65 km in length, drops 1.5 m and has an average flow of 5200 m^3s^{-1}. It is generally a single deep channel with depths from 8-15 m except where obstructed by Stag and Fawn Island, leaving only a few depositional locations before it reaches the St. Clair Delta (Coordinating Commitee on Great Lakes Basic Hydraulic and Hydrologic Data, 1998). Upon reaching the St. Clair Delta, flow decreases and the river splits into an expanse of meandering channels averaging 11 m in depth while shallow bays create depositional zones and complex shoreline of islands covering 80 km^2 (Szalinska et al., 2007). The eastern side of the delta (Chenal Ecarte, Johnston Channel) are narrow, shallow waterways carrying lower water volumes. The Western side of the delta (North, Middle and South Channels) account for most volume to Lake St. Clair (Thomas et al., 2006). Lake St. Clair is shallow averaging only 3.7 m except where bisected by the 8.3 m shipping channel. The lake is essentially divided from the southwest to the northeast by the channels cold water plume which attenuates cross mixing as water moves to the Detroit River (Forsythe et al., 2016). The Detroit River is 51 km in length, drops 0.9 m and has an average flow of 5240 m^3s^{-1} (Szalinska et al., 2013). The upper portion of the

Detroit River is heavily channelized and narrow containing two islands (Belle Isle and Peche Island) as the only obstructions. The lower river transforms into an abundance of large and small islands breaking the river into channels, bays and harbours with the average depth decreasing to 3 m except for the dredged navigational channels (Szalinska et al., 2013). The HEC runs through both highly urbanized, highly industrialized as well as agricultural areas. The Detroit River and St. Clair River AOC's as well as Lake St. Clair receive pollution inputs currently and historically from a complex array of point, non-point, tributary and upstream sources (Szalinska et al., 2006). This complex array is further complicated from inputs entering the system through two additional AOC's the Clinton and Rouge Rivers which drain into the corridor.

3.2.2 - Sample Collection and Laboratory Analysis

Using a random stratified sampling design, six separate surveys were completed throughout the HEC by the Great Lakes Institute for Environmental Research over the 1999-2014 time period. The sampling protocols for the 2013-2014 survey are outlined in Chapter 2 of this thesis while sample site locations across surveys are identified in Figure 2.1.

Sample collection and processing of the 2013-2014 survey were developed for consistency with past published HEC surveys. Following collection of 2L from each location by petit ponar, samples were mixed to ensure homogeneity where they were split for analysis of grain size, loss on ignition (LOI) and priority chemicals including metals, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and

organochlorine compounds (OCs). Grain size distribution was quantified using sieve analysis performed on pre-dried (110°C overnight) sediment samples according to (Szalinska et al., 2007, 2006). LOI was performed as described by Drouillard *et al.* (2006). All chemical constitutes were analyzed on sieved sediments after passing through a 2 mm stainless steel sieve.

Metals were evaluated using strong extractions as described in (Szalinska et al., 2006). Briefly, approximately 3 g of wet sediment sample was placed into a 125ml Erlenmeyer flask. Seven ml of concentrated nitric acid (ACS grade) was added and allowed to stand for 30 minutes after which 21 ml of concentrated hydrochloric acid (ACS grade) was added. The digesta was heated to 100˚C for 5 hours, allowed to stand until room temperature was achieved and transferred into dry pre-weighed 125ml LDPE nalgene bottle after passing through Whatman # 4 filter paper (Nalgene from Fisher Scientific, Toronto, ON). The digesta was brought to a sample weight of 100 g with purified Millipore water. Metal concentrations were evaluated using an inductively coupled plasma optical emission spectrometer (ICP-OES) (1999-2012 used a model: IRIS #701776, Thermo Jarrell Ash Corporation; 2013-2014 used a 700 Series, Agilent Technologies ICP-OES instrument) both under similar protocols and quality control procedures. Metals included both priority chemicals such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) as well as non-priority chemicals aluminum (Al), calcium (Ca), cobalt (Co), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na) and vanadium (V). Certified reference materials (NRC S-MESS3 and S-PACS2), along with three method blanks were analyzed

with every 40 samples including one duplicate sample chosen at random Both replicate samples as well as duplicate samples from every 5th sampling location were run to ensure reproducibility of results. Detection limits for metals were in the range of 0.005-14 $\mu g \cdot g^{-1}$. Sample recoveries of certified standards were typically in the 85%-110% range across trace elements. Total Hg analytical methods are described in Chapter 2 of this thesis. Detection limits for Hg were 0.007-0.03 $\mu g \cdot g^{-1}$. The recoveries of certified NIST standards run with batches of samples were in the range of 90-108%.

Organic contaminant extraction was performed according to Drouillard et al., 2006. Twenty grams of wet sediment was dried with 100 g anhydrous sodium sulphate (ACS grade, BDH, ON) and ground using a glass mortar and pestle. The homogenate was transferred to a glass thimble, spiked with surrogate standards (PCB34, BDE71) and extracted using 300 ml Acetone: Hexane (1:1 volume; OmniSolv-grade, VWR, ON) by Soxhlet apparatus for 24h. Extracts were back extracted using a separatory funnel containing 20% sodium chloride in 200 ml Millipore water and hexane over three solvent washings to remove acetone. Hexane extracts from each wash were collected, combined and eluted through a glass chromatography column (35 cm x 2.5 cm) containing 80 g anhydrous sodium sulphate and further eluted with 200 ml of hexane. The sample was roto evaporated to 2 mL prior to cleanup. Cleanup was performed by transferring the extract to a florisil column (35 cm x 1 cm column prepared with 6 g of activated florisil; VWR, ON, Canada) and 2 cm of sodium sulfate wet packed in hexane. The analytes were eluted from the column with 50 mL hexane (Fraction 1) followed by 50 mL of 15% dichloromethane (DCM):85% hexane (Fraction 2). Following elution, 5ml

of isooctane (OmniSolv, VWR, ON) was added to each faction as a keeper solvent and extracts were rotoevaporated to 2ml. To remove sulphur, activated copper (0.2-0.5g) was added to each clean-up extract and allowed to sit overnight. In cases where copper was found to be blackened, the processes was repeated until added activated copper failed to further react. Extracts from each fraction were transferred into a separate 2 mL GC-autosampler vial for GC analysis.

Gas chromatography analysis was performed using a Hewlett-Packard 5890 chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD), a 60m x 0.25 mm x 0.1 μm DB-5 column (J&W Scientific; CA, USA) and Hewlett-Packard 7673a auto sampler as described in Lazar et al. (1992). Each florisil fraction was injected separately and examined for their associated contaminants to quantify their respective areas on the chromatograms. Where analytes were found in both fractions, their areas were added prior to concentration calculation. Additional QA procedures involved running duplicate standards and iso-octane blanks between samples within GC runs. Forty individual and co-eluting PCB congeners from tri- to nona-chlorobiphenyls were characterized by retention time and quantified using working standards derived from a certified standard mixture (Quebec Ministry of Environment PCB congener mix; Accustandard, New Haven, CT). The PCB congeners commonly available across individual surveys included IUPAC #s: 28, 31, 44, 49, 52, 70, 74, 82, 87, 101, 99, 105, 110, 118, 127, 128, 132, 138, 149, 151, 153, 157, 170, 171, 158, 180, 183, 187, 194, 195, 206, 208 with Sum PCBs calculated as the sum of the above congeners. Organochlorine compounds (OCs) were characterized on the same extracts using retention time in

relation to a working standard generated from a certified standard (Custom OC-Pesticide mix from AccuStandard, New Haven, CT). OC pesticides quantified included: hexachlorobenzene (HCB), octachlorostyrene (OCS), transnonachlor, and p,p'-dichlorodiphenyldichloroethylene (p,p'-DDE).

Following injection onto GC-ECD, fractions 1 and 2 were combined and added to a new GC-sample vial for analysis of PAHs. PAH analysis was performed using a Hewlett-Packard 5890/5979 gas chromatograph with a mass selective detector (GC-MSD) in selective ion monitoring mode, a 60m x 0.25 mm x 0.1 µm DB-5 column and 7673 autosampler. Further details of GC conditions, oven program and ion windows are described elsewhere by (Lazar et al., 1992). Analysis of 15 priority PAHs included: naphthalene (NA), acenaphthylene (AL), acenapththene (AE), fluorine (FL), phenanthrene (PHE), anthracene (AN), fluoranthene (FLT), pyrene (PY), benzo(a)anthracene (B(a)A), chrysene/triphenlyene (CT), benzo(b)fluoranthene (B(b)F), benzo(a)pyrene (B(a)P), indeno(1,2,3,-c,d)pyrene (IP), dibenzo(a,h)anthracene (D(a,h)A), and benzo- (g,h,i)perylene (B(ghi)P). Identification came from retention time and by monitoring the major ion in the molecular ion cluster for each compound. PAHs were quantified based on a 5 standard calibration curve using working standards generated from a certified standard (PAH mix standard from AccuStandard, New Haven, CT).

For organic contaminants, each batch of 5-7 samples was accompanied by co-extraction of a method blank and certified reference sediment (NIST - SRM 1944) to monitor laboratory performance and ensure quality assurance. For all contaminants, Individual surveys detection limits, blank corrections and quality assurance parameters

can be found elsewhere (Drouillard et al., 2006; Szalinska et al., 2013, 2007, 2006). The current survey detection limits were in the range of 0.01-0.15 ng g^{-1} for PCBs, 0.02-0.12 ng g^{-1} for PAHs, and 0.01-0.06 ng g^{-1} for OCs. Surrogate standard recoveries were between 70-140% for PCB 34 and BDE 70. Where recoveries were less than 70%, the sample was re-run until satisfactory recoveries were obtained. Quality assurance procedures for recoveries of PCBs, selected OCs and PAHs in the certified reference material, run with each batch, required that recoveries were within 2 standard deviations of their certified values. Failure to comply with the above rule required that the entire batch be re-analyzed until compliance was achieved.

3.2.3 - Data Analysis

Due to variation of data availability between surveys, some adjustments to standardize common chemical parameters (e.g. list of PCB congeners) into one database was required. The database also included all chemical parameters as described in the analytical section above, along with bottom velocity at each site generated from the Anderson et al., 2010 model using 2014 data and LOI representative of percent organic matter content. All data was tested for normality using Shapiro-Wilk's test and log normalized where necessary before analysis. All analysis including the Hot spot analysis was conducted on normalized data. Owing to the commonality of log normal distributions, measures of central tendency reported in the text are geometric means and 95% confidence interval of the mean unless otherwise indicated.

Principal components analysis (PCA) was performed using a correlation matrix to determine pollutant intercorrelations and reduce the dimensionality of the dataset to facilitate statistical power of regional (waterbody) and temporal (period) comparisons. Thirty sample sites were discarded from the PCA analysis because they were incomplete with respect to the analysis of all chemical groups. Chemicals having a detection frequency of less than 60% across sample locations were removed from the PCA owing to the necessity of requiring a complete data matrix for the PCA. For the non-excluded chemicals, non-detections were replaced with the chemical detection limit. During interpretation of the PCA, chemicals with loadings onto a given PCA axis greater than 0.6 were considered to be strongly affiliated with that axis, those with loadings >0.7 were considered very strongly affiliated with the axis. An initial PCA was performed consisting of LOI, bottom water velocity, individual PCBs, PAHs, OCs and metals. On examination of the initial PCA results, it was observed that all PCB congeners behaved similarly, all PAHs behaved similarly, most priority metals loaded similarly while OCs showed different loadings across axes. Non-priority metals, i.e. those without associated sediment quality guidelines, generated no strong loading patterns onto any axis or were distributed mainly to lesser PCA axes (beyond PCA #4). To further simply the analysis, a second PCA was then performed using a truncated data set. In this case, individual PCBs were removed and replaced with sum PCBs as was the case for PAHs. Finally, the non-priority metals were excluded. Principle components analysis was completed using PAST3 software (Hammer et al., 2001).

General linear models (GLM) were used to test for differences in log transformed chemical concentrations for selected chemicals for temporal and spatial differences between waterbody, country, time period and their interactions. Chemicals used in the GLM were selected based on their representativeness as identified by the PCA. Where interactions were non-significant, they were removed and the GLM re-tested to increase statistical power. Tukey's post-hoc comparisons were used to test individual groups within each treatment. A probability of <0.05 was used to test for significant differences between groups. GLM and Tukey's tests were completed on log transformed data using SYSTAT 13 statistical software.

Getis Ord local statistics were performed in order to designate hot (significantly contaminated) and cold (significantly lower than mean HEC contamination) zones using a user-defined matrix described in Chapter 2. Both hot and cold zones for contaminants of interest may not be representative of harmful levels with repect to pollutants but represent concentrations above/below the threshold of distrbutional values, designating them hot spots/cold spots. Briefly, Getis Ord analysis was performed using the Hot Spot Analysis Tool (ESRI, 2016) in ArcGIS version 10.3. This technique establishes clusters of sampling locations that demonstrated significantly higher or lower concentrations relative to the system wide mean. The Gi* statistic operates by generating a new 'neighbor influenced local mean concentration' for each sample location based on the measured value at the location as well as the values of its neighboring sites specified by a defined spatial relationship. The neighbor influenced local mean is then compared against the corridor wide distribution of concentrations

and assigned into three categories: hot, cold or intermediate. A distance threshold of 5000 m was used in the GI^* statistic assessment. This specifies that all neighbor sampling locations within 5000 m of a given station are considered in the estimation of the neighbor influenced local mean. However, given that the HEC is a flowing system and broken up by island barriers, a user defined matrix was applied in order to censor neighbor stations that were deemed to be not physically connected to a given sampling location. Three rules were used to censor neighbors: i) neighbors that were on opposite sides of large islands or land barriers; ii) neighbours that were found on the opposite sides of a navigational channel or iii) neighbors that were downstream of the station relative to the major direction of water flow. Neighbors conforming to the above rules were assigned a weight of zero in the neighbour influenced local mean calculation, i.e. they were excluded. All other neighbours were given an equal weight to the neighbour influenced local mean calculation. A distribution confidence interval (CI) of 90% was utilized to classify neighbor influenced local mean concentration values for each site. Stations exceeding the upper 90% CI were designated as hot, those less than the lower 90% CI were designated as cold and those within the CI were assigned as intermediate. Given that most chemicals demonstrated a log-normal distribution, the Getis-Ord analysis was performed on log transformed data as opposed to raw data. An interpolation map of the Getis-Ord categories was then created by overlaying a 250 x 250 m grid on the HEC and assigning each cell in the grid a category (hot, cold or intermediate) with the Spatial Join tool based on its nearest cell allocation. Cells of the same designation were merged using the Dissolve tool to generate a map based on the

three respective zones. Evaluation of temporal differences of Hot and Cold zone locations was performed to assess if shifting or change in location of major hot and cold spots were observed between the Early and Late time periods.

System-Wide mass balance of selected contaminants was calculated for surface sediments similar to that described by Szalinska et al. (2013). The Detroit River and St. Clair river were each split into 6 zones; upstream, midstream and downstream reaches that were further split into Canadian and U.S. sides. Both Lake St. Clair and the St. Clair Delta were split into Canadian and U.S. sides. For each specific zone a mass balance was calculated according to:

$$M = C \cdot \rho \cdot A \cdot D \quad (1)$$

Where M is the total mass of chemical in each given zone (kg). *C* represents the mean chemical concentration in that zone (kg/kg dry sediment weight), *p* is the dry bulk density (kg dw/m^3), *A* is the surface area of each zone (m^2) and *D* represents the depth (m) of sampled surface sediments (fixed at 0.1 m for all sample stations). The assignment of bulk sediment densities was according to Verstraeten and Poesen (2001) as 1378 kg/m^3 for particles <0.150 mm, and 1426 kg/m^3 for particles >0.150 mm estimated for each sample location based on measured grain size distributions. Area measurement of each strata were computed using ArcGIS (ESRI, 2016) by splitting a high-resolution shoreline polygon of the HEC into the respective zones of analysis. The "Calculate Geometry" tool was used to calculate area in (m^2). Chemical mass balance in each water body was determined by summing the chemical masses in each zone. Error

Estimates for chemical mass balances was estimated by Monte Carlo procedure as described in Szalinska et al. (2013). The mean and standard deviation values of zone specific chemical concentrations, sediment moisture contents, and dry bulk density were incorporated as model inputs having error. Monte Carlo simulations were performed using Oracle Crystal Ball Software under an assumed a log normal distribution of each variable and run for 100,000 model trials. Geometic mean mass balance and standard deviations were subsequently computed from the Monte Carlo trial values.

3.3 - Results

Grain size analyses revealed that sediments sampled from the upper and midstream sections of both the St. Clair River and Detroit River were coarser then sediments taken from the downstream reaches of each river as well as the St. Clair delta and Lake St. Clair. Particles in the upper and midstream portions were generally gravelly and sandy with lower reaches of the rivers generally consisting of fine sand to clay fractions (<0.106 mm). The samples containing the most fines (silt to clay) (<0.063mm) were found in Lake St. Clair and downstream Detroit River, respectively. Organic carbon content as determined from LOI ranged from 0.2% to 19.2% with the highest observed values located in the Detroit River (Table 3.2). LOI in the Detroit river was significantly higher ($p < 0.01$; Tukey's HSD) in comparison to the other systems, whilst the St. Clair River and Lake St. Clair did not show any significant differences. The Detroit River showed significantly higher LOI in the late years ($p < 0.001$; Tukey's HSD), while the St.

Clair River ($p > 0.05$; Tukey's HSD) and Lake St. Clair ($p > 0.05$; Tukey's HSD) were not significantly different between sample periods.

Among the investigated contaminants, priority metals (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Zn) as well as sum PCBs and sum PAHs were previously identified as having exceedances of sediment quality guidelines in the HEC (Drouillard et al., 2006; Szalinska et al., 2013, 2007). It is important to note that some metal contaminants such as arsenic and iron can be a product of both natural as well as anthropogenic sources and will be evaluated together in relation to the sediment guidelines. Sediment concentration data across sampling stations and time periods for the full dataset were contrasted against consensus based sediment quality guidelines for the purpose of this study (MacDonald et al., 2000) in relation to threshold effect concentration (TEC) values and probable effect concentration (PEC) values. Table 3.1 summarizes the percentage of exceedances above TEC/PEC thresholds for each river system. For exceedences of PEC, Hg was the only contaminant to exceed PEC thresholds in both the St. Clair River (1.3%) and Lake St. Clair (8.5%) in early survey years. In later years Hg exceedences of PEC increased to 3.2% in St. Clair River but was 0% in the lake. A small number of stations (0.6%) exceeded PEC for PAHs in the St. Clair River during the late period. The Detroit River exceeded PEC thresholds for each contaminant except As, ranging from 1.4-7.5% over both time periods. Sum PAHs had the highest percentage of samples locations exceeding PEC values. The percentage of PEC exceedances remained similar for the Detroit River between the two time periods.

Table 3.1 Max concentrations and Probable effect concentration (PEC) exceedences by each waterbody and the early and late time period. Concentrations are expressed in ug/g dry weight for metals and PAHs and ng/g for PCBs.

Element (TEC, PEC)	St. Clair River						Lake St. Clair						Detroit River					
	Early			Late			Early			Late			Early			Late		
	Max	% >TEC	% >PEC	Max	% >TEC	% >PEC	Max	% >TEC	% >PEC	Max	% >TEC	% >PEC	Max	% >TEC	% >PEC	Max	% >TEC	% >PEC
Sum PCB (59.8, 676)	54.6	0.0	0.0	248.5	5.4	0.0	54.6	0.0	0.0	36.7	0.0	0.0	**1319.2**	27.5	**2.74**	**1927.3**	29.9	**2.1**
Sum PAHS (1.61, 22.8)	11.4	8.1	0.0	47.4	40.5	0.6	3.1	8.2	0.0	7.8	6.1	0.0	**202.2**	46.7	**15.75**	**217.8**	45.5	**7.5**
As (1.6, 2.2)	5.5	0.0	0.0	**18.0**	27.0	0.0	6.7	0.0	0.0	17.3	14.3	0.0	**57.5**	31.7	**8.22**	14.5	0.6	0.0
Cd (0.99, 4.98)	1.0	2.7	0.0	3.2	44.6	0.0	0.6	0.0	0.0	3.4	34.7	0.0	**7.4**	51.5	0.68	**8.1**	52.1	**5.5**
Cr (43.4, 111)	44.4	1.4	0.0	56.0	10.8	0.0	20.1	0.0	0.0	30.7	0.0	0.0	**121.7**	11.4	**0.68**	**217.7**	9.6	**2.7**
Cu (31.6, 149)	44.7	4.1	0.0	66.0	4.1	0.0	39.1	6.1	0.0	15.6	0.0	0.0	**216.4**	38.3	**2.74**	**599.3**	23.4	**3.4**
Fe (20000, 40000)	34600.0	6.8	0.0	33700.0	21.6	0.0	19380.0	0.0	0.0	16443.0	0.0	0.0	**61685.9**	37.7	**6.16**	**92079.3**	31.7	**4.1**
Hg (0.18, 1.06)	2.7	51.4	**1.3**	2.9	71.6	**3.2**	1.8	46.9	**8.5**	0.8	42.9	0.0	**6.3**	49.1	**5.48**	**9.1**	35.3	**1.4**
Ni (22.7, 48.6)	36.6	5.4	0.0	41.0	20.3	0.0	22.5	0.0	0.0	19.4	0.0	0.0	**66.4**	41.3	**4.79**	**134.0**	27.5	**5.5**
Pb (35.8, 128)	16.0	0.0	0.0	185.0	4.1	0.6	16.1	0.0	0.0	11.5	0.0	0.0	**686.1**	14.4	**4.79**	**769.4**	13.2	**3.4**
Zn (121, 459)	102.2	0.0	0.0	178.0	1.4	0.0	69.8	0.0	0.0	50.3	0.0	0.0	**741.1**	25.7	**1.37**	**1731.6**	18.6	**4.1**

TEC- Threshold Effect Concentration, PEC - Probable Effect Concentration; bolded - Max observed values for that contaminant, Max percentage of PEC exceedances

Table 3.2 Priority Contaminant concentrations by waterbody for the Huron-Erie Corridor separated by the early and late time periods. Concentrations are expressed as a geometric mean and 95% confidence interval in ug/g dry weight for metals and PAHs and ng/g for PCBs

	SCR +DELTA		LSC		DR	
	Early	Late	Early	Late	Early	Late
TOC (LOI)	2.08 (1.81-2.40)	2.12 (1.96-2.29)	1.81 (1.54-2.13)	1.91 (1.67-2.19)	2.44 (2.17-2.74)	3.74 (3.35-4.19)
HCB	3.86 (2.48-5.99)	0.78 (0.56-1.09)	3.21 (2.02-5.08)	0.31 (0.19-0.52)	2.55 (2.00-3.24)	0.65 (0.50-0.85)
OCS	1.32 (0.91-1.90)	0.54 (0.38-0.77)	0.92 (0.49-1.70)	0.41 (0.27-0.62)	0.62 (0.52-0.74)	0.54 (0.43-0.69)
Trans-Nonachlor	0.15 (0.13-0.16)	0.04 (0.03-0.04)	0.12 (0.10-0.15)	0.03 (0.02-0.04)	0.22 (0.18-0.27)	0.07 (0.05-0.08)
p,p'-DDE	0.55 (0.47-0.65)	0.35 (0.30-0.41)	0.79 (0.60-1.03)	0.21 (0.16-0.26)	1.40 (1.14-1.73)	1.27 (1.00-1.61)
Sum PCB	5.1 (4.1-6.5)	6.6 (5.6-7.7)	4.2 (2.9-5.9)	2.9 (2.0-4.2)	19.0 (13.9-25.9)	28.9 (22.2-37.5)
Sum PAH	0.31 (0.22-0.44)	0.65 (0.54-0.78)	0.09 (0.04-0.19)	0.26 (0.28-0.35)	1.80 (1.31-2.48)	2.26 (1.65-3.10)
As	2.3 (2.1-2.5)	4.0 (3.6-4.4)	1.9 (1.8-2.1)	2.9 (2.4-3.4)	5.8 (4.8-6.9)	3.5 (3.3-3.8)
Cd	0.4 (0.3-0.4)	0.5 (0.4-0.5)	0.3 (0.2-0.3)	0.5 (0.4-0.6)	0.9 (0.8-1.1)	1.4 (1.2-1.5)
Cr	8.9 (7.8-10.1)	14.4 (13.2-15.8)	9.4 (8.2-10.7)	13.0 (11.6-14.6)	20.8 (18.9-23.0)	22.9 (20.3-25.9)
Cu	8.5 (6.9-10.6)	9.6 (8.7-10.7)	12.3 (10.1-14.9)	5.6 (4.8-6.7)	26.4 (23.6-29.5)	20.7 (17.6-24.3)
Fe	9003 (8067-10047)	9355 (8571-10212)	8580 (7633-9645)	7698 (6914-8571)	16947 (15698-18296)	17069 (15451-18856)
Hg	0.17 (0.13-0.22)	0.08 (0.07-0.11)	0.17 (0.11-0.26)	0.10 (0.07-0.13)	0.14 (0.11-0.17)	0.15 (0.13-0.18)
Ni	9.7 (8.5-11.0)	9.4 (8.5-10.3)	9.2 (8.0-10.6)	6.5 (5.7-7.3)	19.9 (18.2-21.7)	17.8 (16.0-19.6)
Pb	4.3 (3.8-4.9)	6.2 (5.6-6.8)	4.4 (3.6-5.4)	4.2 (3.7-4.8)	14.0 (11.9-16.5)	16.0 (13.5-18.9)
Zn	36.5 (32.6-40.8)	34.7 (32.1-37.6)	31.8 (27.4-36.8)	24.8 (22.2-27.6)	70.0 (61.7-79.4)	76.2 (65.8-88.2)

TEC exceedences were most prominent for Hg in the St. Clair River and Lake St. Clair reaching 70% of sites exceeding TEC in the later years for the St. Clair River. TEC thresholds were surpassed for a higher percentage of stations in the later survey years for all systems. The St. Clair River ranged from 1.4 to 71% of sites above TEC for all contaminants, while Lake St. Clair only passed thresholds for PAHS, As, Cd, and Hg. The Detroit River had the highest percentage of TEC exceedances of the systems, ranging from 9.6 to 52%, excluding As which only had 0.6% of sites above the TEC.

PCA analysis was performed to reduce the dimensionality of the contaminant concentration dataset and to group chemicals into those displaying similar behavior. The PCA yielded three principal components that explained 45.5, 10.4 and 7.6% of the variance. The eigenvalues of the first 3 axes were all above 1. Chemical loadings, expressed as correlation coefficients, are summarized in Table 3.3. PCA axis 1 was very strongly associated ($r > 0.7$) with LOI, sum PCBs, sum PAHs, Cr, Cu, Ni, Pb, Zn and also had strong loads ($r > 0.6$) for trans-nonachlor, p,p'-DDE, Cd, and Fe. PCA axis 2 had strong loadings ($r > 0.6$) for HCB and OCS. Neither Hg or As was found to load strongly (above a correlation of 0.6) onto any PCA axis, although Hg had moderately high loads approaching 0.5 for both PCA 1 and PCA 2. Based on the inter-chemical correlations, selected contaminants were chosen to be of focus for temporal and spatial assessment. The selected contaminants included sum PCBs (representative of Group 1 compounds), HCB (representative of Group 2 compounds) and total Hg. Although Hg did not load strongly onto any PCA, it was selected as a chemical of interest because it is a priority pollutant with a large number of PEC exceedances in sediments of the HEC and

is also linked to several BUIs in the AOCs. PCBs patterns, representative of Group 1 chemicals, by waterbody were found to be significantly different from one another ($p < 0.001$; GLM) and had a rank order of DR > SCR >LSC. However, the GLM contrasts for PCBs showed significant differences ($p < 0.001$; $F=17.205$, d.f. = 1, 629) between time periods as well as significant ($p < 0.001$; $F=110.616$, d.f. = 2, 629) differences between waterbodies as well as a significant ($p < 0.001$; $F=68.678$, d.f. = 2, 629) waterbody x country interaction. Given the significant interaction term, separate GLMs and Tukey's pairwise comparisons were applied to each water body to tease out the effect of country and time period (Figure 3.1). For the St. Clair River, PCB concentrations were significantly higher ($p<0.05$; Tukey's HSD) in Canada compared to the U.S. in the late time period but not-significantly different ($p>0.05$; Tukey's HSD) in the early period. Although PCB concentrations were generally higher in the late time period, they were non-significantly ($p>0.05$; Tukey's HSD) different with time within either jurisdiction. For Lake St. Clair, PCBs were generally higher in Canadian waters compared to the U.S. but such differences were non-significant ($p>0.05$; Tukey's HSD) when each time period was considered separately. Only the late period Canadian waters had significantly higher ($p<0.05$; Tukey's HSD) PCBs then the early period U.S. jurisdiction. There were also no significant differences by time period for individual jurisdictions in the lake. For the Detroit River, PCB concentrations were significantly higher ($p<0.05$; Tukey's HSD) in U.S. waters compared to Canadian waters in each time period. PCBs in each jurisdiction increased slightly in the late time period, but non-significantly ($p>0.05$; Tukey's HSD) so.

Table 3.3 Principal component loadings of contaminants for all years Huron-Erie corridor dataset.

Variable	PC 1	PC 2	PC 3
	45.4%	10.5%	7.6%
LOI	**0.71**	-0.13	-0.33
HCB	0.36	**0.67**	0.04
OCS	0.28	**0.63**	-0.09
transnon	**0.60**	0.10	0.33
DDE	**0.64**	0.20	0.35
sumPCB	**0.79**	0.35	0.19
sumPAH	**0.77**	0.10	0.21
As	0.28	-0.34	0.47
Cd	**0.65**	-0.07	0.16
Cr	**0.84**	-0.24	-0.13
Cu	**0.85**	-0.20	-0.15
Fe	**0.68**	-0.39	-0.14
Hg	0.49	0.53	-0.40
Ni	**0.87**	-0.24	-0.17
Pb	**0.89**	-0.07	0.01
Zn	**0.91**	-0.11	-0.15

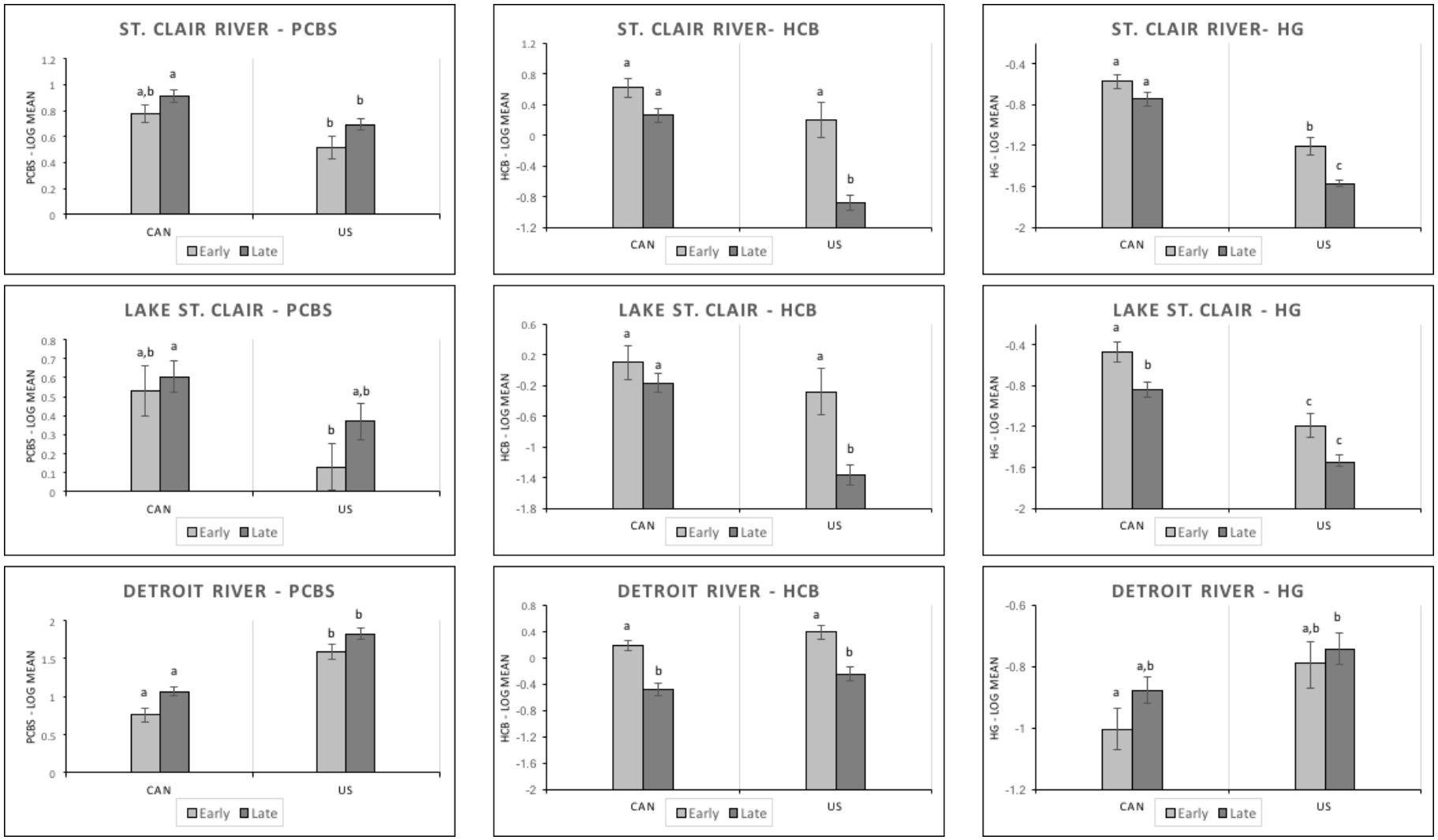

Figure 3.1 GLM contrasts for PCBs (left graphics), HCB (center graphics) and Hg (right graphics) separated by waterbody. Within a graphic, different letter subscripts represent significant differences($p < 0.01$, GLM)

HCB patterns, representative of Group 2 chemicals, had a significant rank order established by GLM of St. Clair River = Detroit river > Lake St. Clair. The GLM contrasts for HCB showed significant differences ($p < 0.001$; $F = 85.398$, d.f. = 1, 625) between time periods and by country ($p < 0.001$; $F = 32.486$, d.f. = 1, 625) as well as significant ($p < 0.001$; $F = 10.208$, d.f. = 1, 625) period x country interaction and a significant ($p < 0.001$; $F= 24.081$, d.f. = 1, 625) waterbody x country interaction. Figure 3.1 summarizes differences in HCB concentrations by time and jurisdiction for each water body. For the St. Clair River, HCB concentrations were significantly higher ($p<0.05$; Tukey's HSD) in Canada compared to the U.S. for the late time period, but not in the early time period. HCB exhibited a significant ($p<0.05$; Tukey's HSD) decrease in concentration through time in the U.S. jurisdiction but not the Canadian jurisdiction. A similar spatial and temporal pattern was evident for Lake St. Clair although concentrations of HCB in the lake were lower than observed for both AOCs. For the Detroit River, HCB concentrations decreased significantly ($p<0.05$; Tukey's HSD) with time in both the Canadian and U.S. jurisdictions but showed no differences ($p>0.05$; Tukey's HSD) between the jurisdictions.

Hg patterns between waterbodies had a significant rank order established by GLM of Detroit River > St. Clair River = Lake St. Clair. The GLM contrasts for Hg showed significant differences ($p < 0.001$; $F=14.572$, d.f. = 1, 626) between time periods, country ($p < 0.001$; $F= 91.578$, d.f = 1, 626) and waterbody ($p < 0.001$; $F=8.091$, d.f = 2, 626) as well as a significant ($p < 0.001$; $F= 10.018$, d.f. = 2, 626) waterbody x time period interaction and a significant ($p < 0.001$; $F= 62.999$, d.f. = 2, 626) waterbody x country

interaction. Given the significant interaction term, separate GLMs and Tukey's pairwise comparisons were applied to each waterbody. Differences in total Hg concentration by time and jurisdiction for each waterbody are summarized in Figure 3.1. For the St. Clair River, Hg concentrations were significantly higher ($p<0.05$; Tukey's HSD) in Canadian compared to U.S. waters at both time periods. There was no significant ($p>0.05$; Tukey's HSD) change in Hg concentration with time in the Canadian Jurisdiction, but Hg concentrations significantly ($p<0.05$; Tukey's HSD) decreased with time in the U.S. Jurisdiction. For Lake St. Clair, Hg concentrations were significantly ($p<0.05$; Tukey's HSD) higher in Canadian waters compared to U.S. waters. Hg concentrations exhibited a significant ($p<0.05$; Tukey's HSD) decrease with time in the Canadian waters of Lake St. Clair but not for the U.S. jurisdiction. For the Detroit River, Hg concentrations were not significantly different between Canadian and U.S. waters when contrasts were restricted to a given time period. However, Hg in the late U.S. time period was significantly ($p<0.05$; Tukey's HSD) higher than the early Canadian time period. Unlike the St. Clair River and Lake St. Clair, the general trajectory was for higher, but not significantly so, Hg levels in the later time period. Overall, the spatial/temporal pattern for both Hg and HCB were very similar to one another for St. Clair River and Lakes St. Clair but the two contaminants diverged from one another in their pattern of contamination for the Detroit River.

Spatial analysis of Hot and Cold zones generated by Getis-Ord analysis was performed for sum PCBs, HCB and Hg in the early, late time periods and combined period data sets (Figures 3.2-3.4). Each figure provides both the local-mean category

generated by Getis-Ord local statistics as well as the interpolated map of Getis-Ord categories across the HEC. Ellipses highlight major hot and cold zones commonly observed for early and late time periods. For PCBs, hot zones were identified predominantly on the U.S. side of the Detroit River extending from the upstream (downstream of Belle Island) through the midstream and most of the way downstream along the U.S. shoreline into Lake Erie (Figure 3.2). Canadian waters of the Detroit River remain predominately intermediate in concentrations with some local cold sites identified in the early years. Major cold zones in the HEC are observed where the St. Clair Delta meets Lake St. Clair in both jurisdictions, extending into the center of the lake (early period), and where Lake St. Clair meets the headwaters of the Detroit river above Peche Island. Sporadic cold sites are identified in portions of the U.S. St. Clair River and in the Detroit River. There was notable variation in the location of major cold zones for Lake St. Clair between the early and late periods. The U.S. center cold zone of Lake St. Clair from the early period reverts to intermediate in the late period. A small cold zone on the Canadian south shore is also lost in the late period. The combined early/late Getis-Ord figure integrates the cold zone differences between the two-time periods but shows little variance in the distribution of hot spots along the U.S. side of the Detroit River.

Hot and Cold zone analysis of HCB exhibited a different pattern then PCBs. Commonly observed HCB hot zones in both years were at the downstream end of the U.S. side of the Detroit River (downstream of Trenton Channel) and the midstream Canadian portion of the St. Clair River in the vicinity of Stag Island (Figure 3.3).

Additional, non-stable hotspots in time were observed in the St. Clair Delta. Large Commonly observed cold zones were found on the U.S. side of Lake St. Clair and small sporadic cold zones on the U.S. nearshore side of the St. Clair river and distributed at individual locations in the Canadian Detroit River. There was greater variance in locations of hot and cold zone regions downstream of the St. Clair Delta on the Canadian side as denoted by dashed ellipse in Figure 3.3. The combined early/late Getis-Ord figure integrates the cold zone differences between the two time periods, similar to that observed in the PCB combined map. It combines the areas indicated by the dashed ellipse but remains identifying both hot and cold regions within the area. Distribution of hotspots within the two AOCs shows little variance.

Hg followed a similar overall spatial pattern of hot and cold zones within the HEC as HCB. Temporally consistent hot zones were observed on the U.S. side of the Detroit River downstream of Trenton Channel, and in small localized hotspots in the Detroit River midstream. Common Hg hot zones in the St. Clair River was upstream and downstream of Stag Island on the Canadian side of the AOC and for the South Channel of St. Clair Delta. Common cold zones between time periods were located in the northeastern portion of Lake St. Clair and the mouth of the Detroit River. Similar to HCB, the dashed ellipse of Figure 3.3 highlights a portion of the Canadian St. Clair Delta/Lake St. Clair confluence which varied in hot/cold zone delineation between the time periods. This section was designated hot in the early period and reverted to intermediate in the late period. This difference was attributed to two sampling locations each completed as triplicated stations during the early and late period surveys of the Walpole Delta (2005

and 2012). A two-sample t-test found significantly lower values in the late survey at both locations ($p < 0.01$, $t = 10.68$; d.f. = 4 and $p < 0.01$; $t = 6.06$; d.f. = 4) while other locations also replicated in the Walpole Delta surveys did not exhibit significant change. However, the low sample density and high dispersion of samples, particularly in the Lake St. Clair makes the interpolation more prone to artifacts. For the Detroit River, there were also differences in several local cold zone stations in the upstream and midstream Canadian sections that reverted to intermediate concentrations in the late period. Closer examination of sampling station locations shows that that cold stations from the early time period in this portion of the Detroit River were from the shipping channel. The late time period sampling sites in the same vicinity tended to be categorized as intermediate in concentrations but were located primarily in the Canadian nearshore areas. The channel and nearshore components of these reaches have different sediment characteristics (grain size and TOC) with the channel stations being subject to high scour due to very high water velocities in the shipping channels. Thus, the apparent increase in sediment Hg levels in the upper and middle Canadian reaches of the Detroit River are potentially associated with subtle sample station location difference between the surveys. The combined map for Hg demonstrates a few interesting deviations in hot zone locations from the individual period graphics. The center hot zone of Lake St. Clair identified in the late year survey derived from a single station becomes extended in size for the combined survey based on neighboring high/intermediate concentrations from the early year survey. Similarly, the U.S. downstream hotspot identified in both survey periods becomes extended up through the Trenton Channel in the combined data set.

Two new hot zones also appear in the Canadian side of the Detroit River at the downstream end of Fighting Island and between Bois Blanc Island and Livingston Channel extending into Lake Erie. These hot zone extensions occur because of the increase in sample density and proximity of neighbors with individual Hg concentrations exceeding the 90% CI threshold.

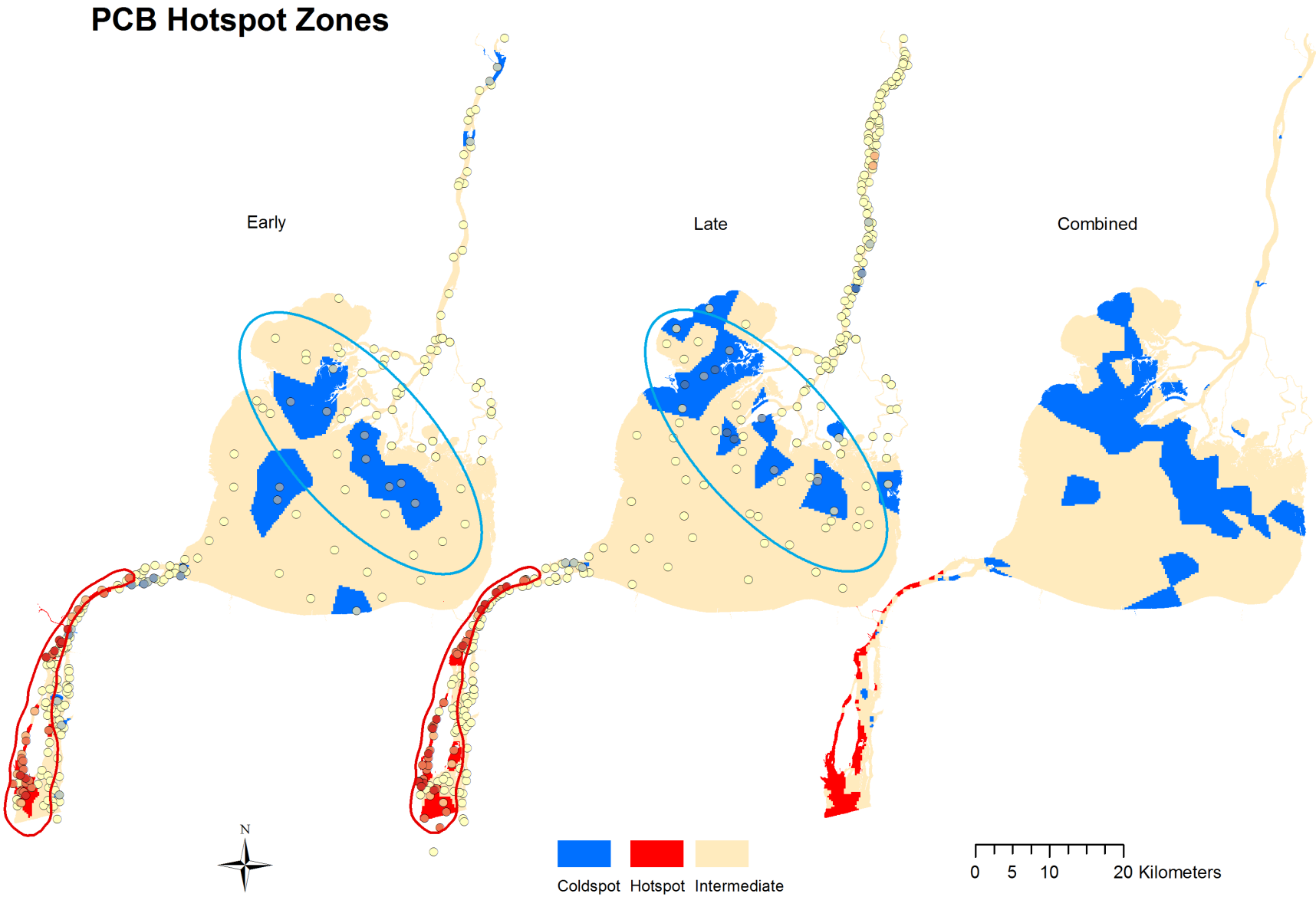

Figure 3.2 Hot and Cold zone contrasts with sample locations included for the Early and Late time periods for PCBs. Red Ellipses represent common hot zones between time periods, blue ellipses represent common cold zones between time periods.

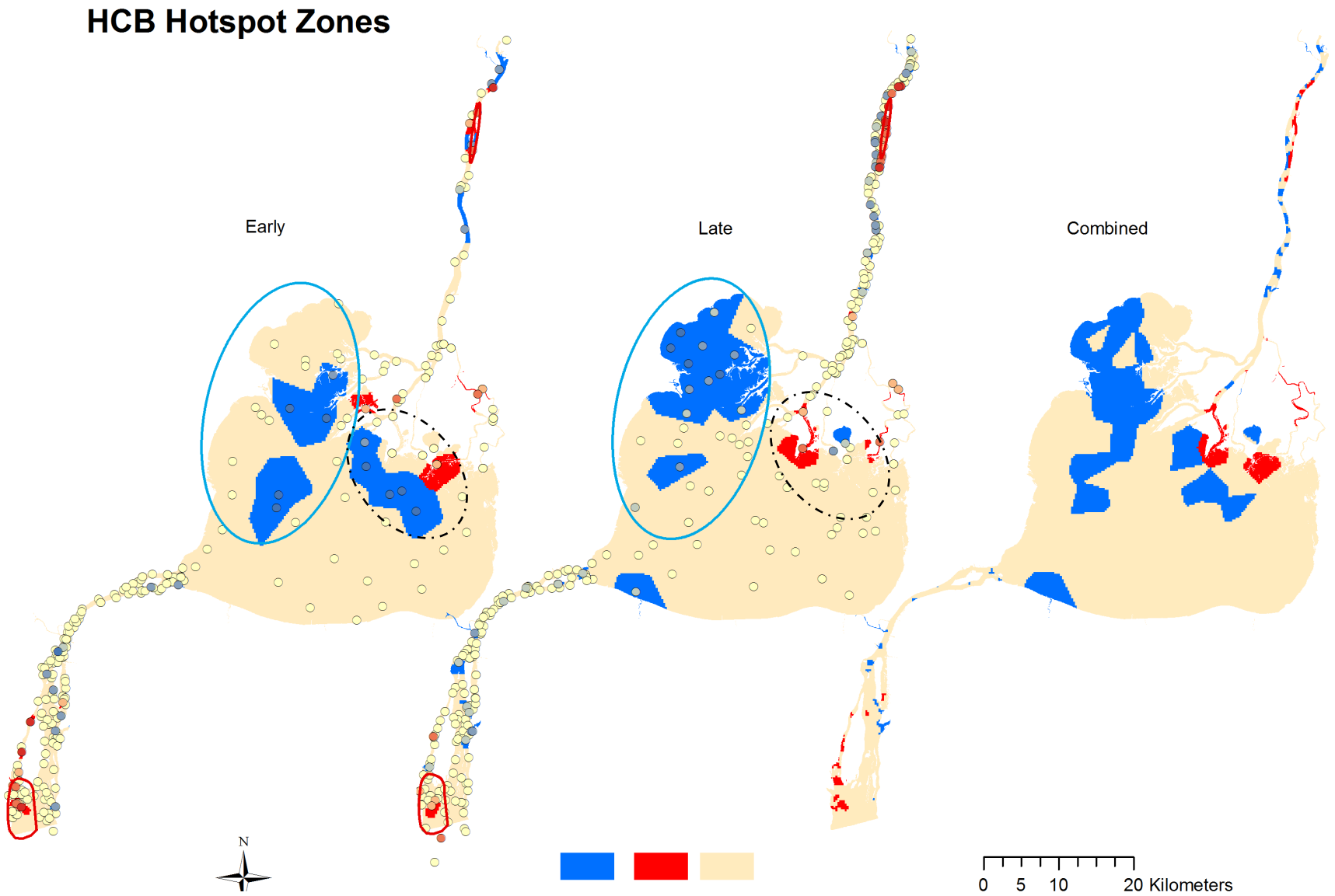

Figure 3.3 Hot and Cold zone contrasts with sample locations included for the Early and Late time periods for HCB. Red Ellipses represent common hot zones between time periods, blue ellipses represent common cold zones between time periods. Dashed ellipse represent a difference between sample years

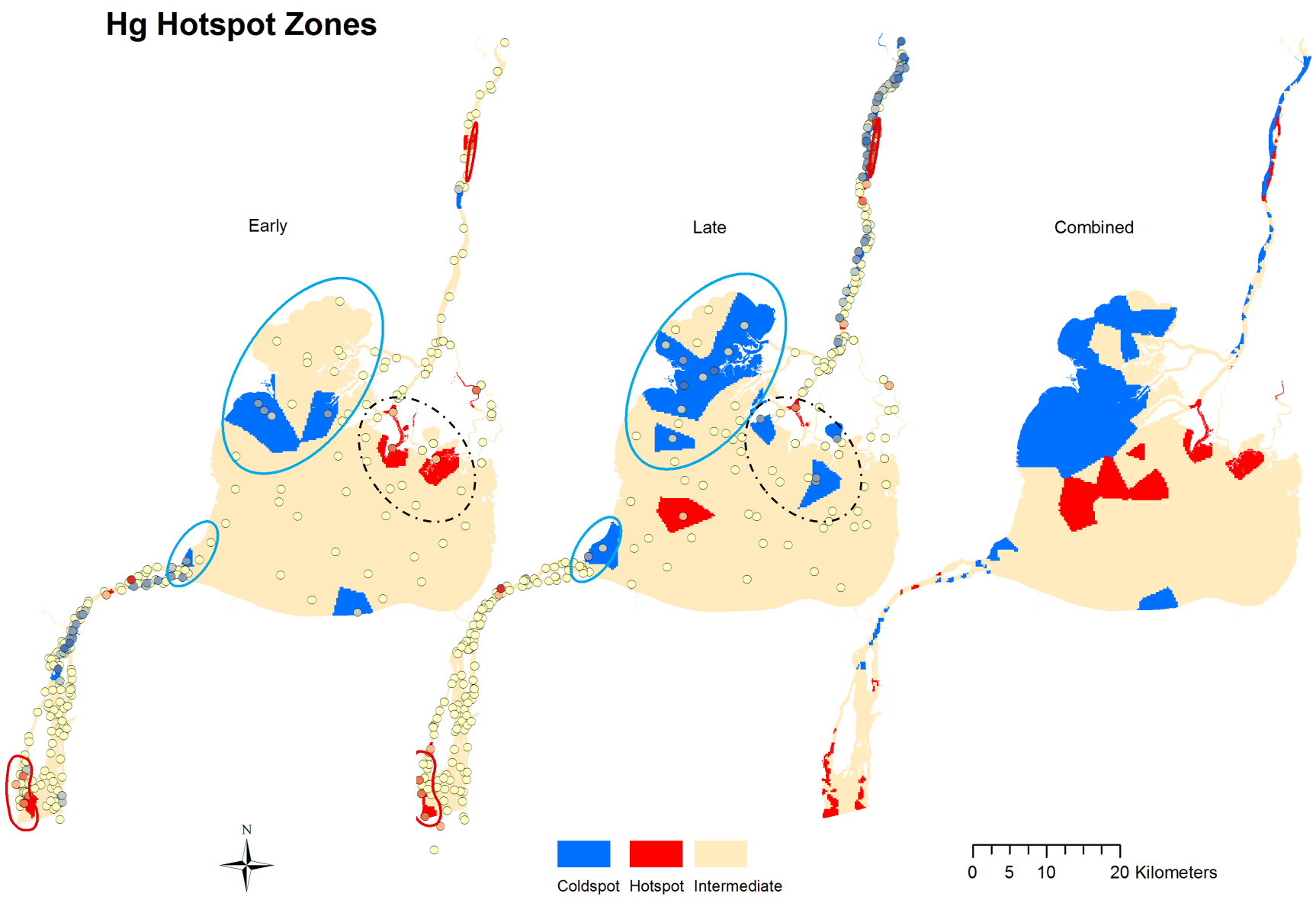

Figure 3.4 Hot and Cold zone contrasts with sample locations included for the Early and Late time periods for Hg. Red Ellipses represent common hot zones between time periods, blue ellipses represent common cold zones between time periods. Dashed ellipse represents a difference between sample years

A major Hg cold zone change between survey periods was observed for the St. Clair river with the late time period having several localized cold spots and large cold zone region identified along most of the U.S. nearshore length that was not observed in the early time period. Similar to the case of Hg in the Detroit River, sample station density and dispersion differences were evident for the St. Clair River between survey time periods. To further highlight this, Figure 3.5 provides an image of the hot and cold zone interpolation maps focusing on the St. Clair River. A major change between early and late time period surveys was the sample resolution which increased from 40 stations allocated for the St. Clair River in 2004 to 100 stations in 2014. The early time period sampling density was comparatively sparse with distances between sampling points as high as 11 kilometers. Local cold zone regions observed in the late time period tended occur within the sampling gaps from the early years and were interspersed with intermediate concentration stations separating them. As such, the significant decline in U.S. Hg levels appears to be an artifact of the large difference in sampling intensity between the two survey periods. Though a similar decreasing concentration trend was not identified by pairwise comparisons on the Canadian side of the St. Clair River, the sampling density differences still explains the difference in zone boundaries observed on the maps and why the hot zone in the later year was much larger. The late period map also corresponds better with the literature which had previously identified the immediate upstream waters of Stag island and its downstream waters as a historical zone of contamination (Marvin et al., 2004a; Richman and Milani, 2010)

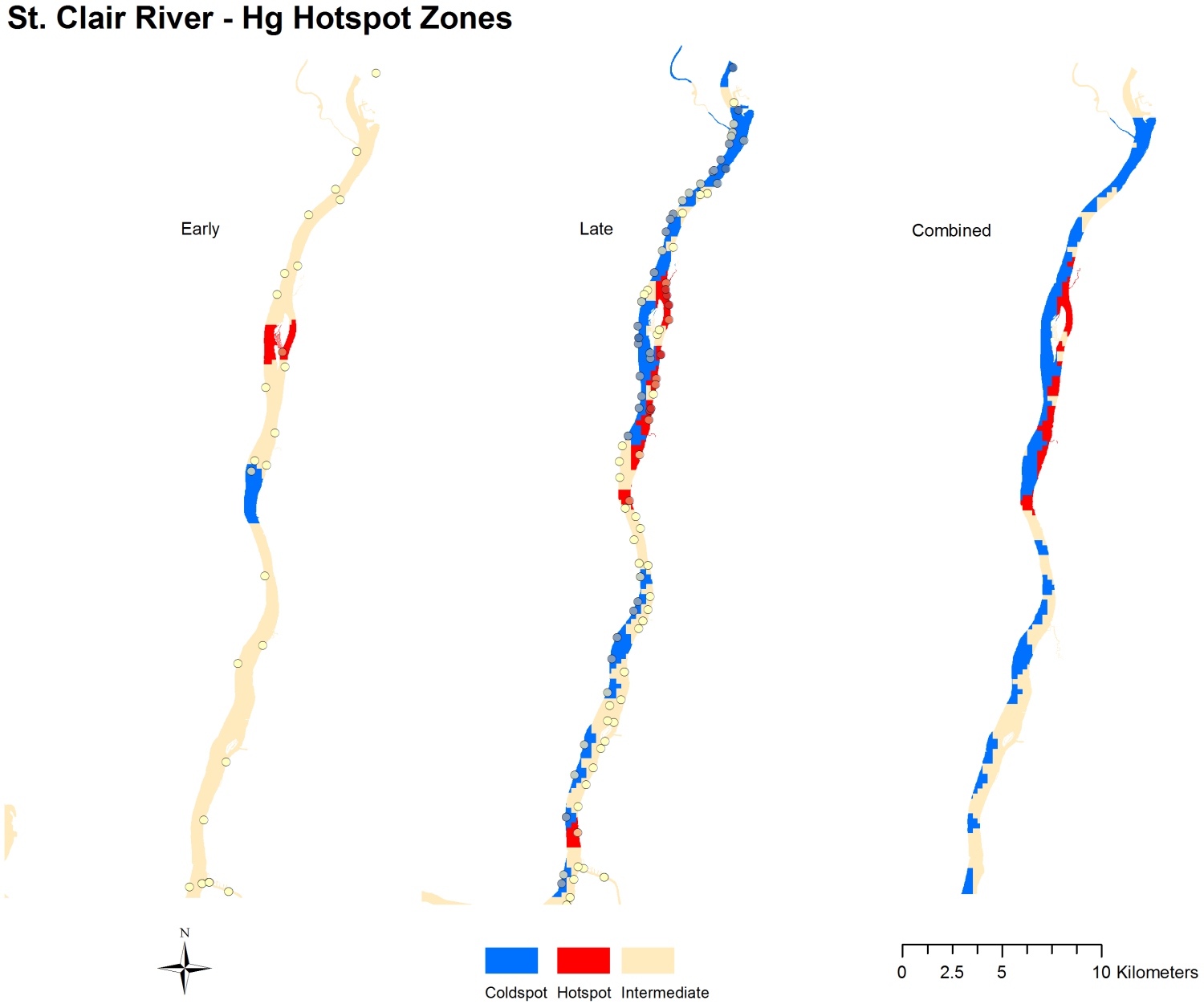

Figure 3.5 Hot and Cold zone contrasts with sample locations included for the Early and Late time periods for Hg in the St. Clair River.

Overall, a comparison of local statistics generated by the Getis-Ord hot/cold zone maps with regional comparisons performed by GLM/Tukey's pairwise comparisons suggests several commonalities between spatial/temporal analysis approaches. Group 1 compounds represented by PCBs exhibited no significant changes with time for each jurisdiction in each waterbody suggesting that the combined corridor map provides the most accurate representation of contamination of this chemical type in the HEC. The highest concentrations within the system were observed for the U.S. portions of the Detroit River as evidenced by Figures 3.1 with PCB hot zones incorporating most of the Detroit River U.S. jurisdiction (Figure 3.3). HCB and Hg had their highest geomean concentrations in Canadian waters of the St. Clair River, but hot zones were much more localized compared to PCBs and group 1 compounds. Thus, HCB and Hg had a much higher degree of spatial heterogeneity compared to PCBs and therefore these contaminants are more sensitive to sampling resolution and sample dispersion differences across temporal comparisons. Indeed the largest temporal differences were noted for HCB, and to a lesser extent Hg, for pairwise comparisons in the U.S. St. Clair River waters and U.S. Lake St. Clair waters. However, the observed decrease in contaminant levels in these sections may be driven by large differences in sampling intensity between survey years, particularly for the St. Clair River. HCB and Hg further diverge in their temporal patterns for the Detroit River. HCB declined in the Detroit River in both Canadian and U.S. waters whereas both Hg and PCBs showed non-significant increasing trends. This implies a possible decoupling of Hg and HCB sources to the Detroit River as opposed to more closely linked sources of the two contaminants

in the upstream waterbodies. Given that significant temporal changes for Hg only occurred in the U.S. St. Clair River reach and this was interpreted to result from sample resolution artifacts, the combined Hg figure is also considered more representative of the true corridor Hg distribution.

Mass Balance estimates for selected priority contaminants (those that did not demonstrate a significant change with time in individual reaches of the corridor) were generated using the combined data set and are summarized in Table 3.4. Iron (Fe) had the greatest mass among priority contaminants in the system with 1.2 million tonnes estimated for the surface sediments of Lake St. Clair. Other metals such as Cu, Zn, Pb ranged from 130-1500 tonnes in the AOCs and slightly higher in the lake ranging from 682-3938 tonnes owing to its ten-fold larger surface area. Total Hg masses ranged from 4-8 tonnes in the AOCs and 49 tonnes in the lake. Comparison of the AOCs show higher mass estimates for all contaminants in the Detroit River, except for Hg which was higher in the St. Clair river. One important note is that sum PCBs did not include all 208 congeners so the mass estimate may be an underestimate.

A second mass balance was completed on selected hot zone boundaries for PCBs and Hg to compare with the system wide mass balances. For PCBs, the large hot zone area encompassing the majority of the U.S. side of the Detroit River was used and for Hg the smaller downstream of Trenton Channel, Detroit River hot zone and the midstream Canadian St. Clair River hot zones were evaluated. The Detroit River PCB hot zone represented a significant proportion of the Detroit River covering 37% of the total area. The mass balance for PCBs was estimated at 0.75 (0.62-0.91) tonnes which represents

67% of the total mass of PCBs present in surface sediments of the Detroit River and 43% of the total mass of PCBs present throughout the entire HEC. Given that the proportion of PCB mass in this section of the river exceeds its areal contribution by almost a factor of 2, removal of contaminated sediments from this hot zone would have a direct impact on the system mass balance.

For Hg, the three selected hot zones were much smaller in their respective areas in the AOCs compared to the extensive PCB hotzone. The Trenton Channel, Detroit River, hot zone covers roughly 11% of the AOC area and had a mass balance estimate of 0.90 (0.80-1.01) tonnes in the hot zone. This represents 18% of the total Hg mass estimated for the Detroit River and 1.44% of the total Hg mass in the HEC. The St. Clair River Hg hot zone represents 1.9% of the total river area including the delta channels. It was found to contain 0.20 (0.14-0.29) tonnes of total Hg representing 2.4% of the total Hg mass present in the St. Clair River and less than 0.3% of the total Hg mass in the HEC. The Lake St. Clair Hg hot zone in the center of the lake represents 6.5% of the total lake area. It was found to contain 48.69 (33.10-71.62) tonnes of total Hg, representing 98.5 % of the total mass observed in Lake St. Clair and 78% of the total Hg mass in the HEC, due to the much larger area then each of the river systems. Given the areal and mass proportions of the three Hg hot zones, remediation of the Lake St. Clair hot zone and/or Detroit River hot zone would provide greater value in terms of achieving a system wide change in Hg mass balance than the St. Clair River zone.

Table 3.4 Mass Balance for selected priority contaminants in the surficial sediment of the Huron-Erie Corridor. Waterbody contaminant mass (tonnes) expressed as a geometric mean estimate (95% confidence interval)

Element/Chemical	**St. Clair River**	**Lake St. Clair**	**Detroit River**
Cd	9.5 (8.9-10.2)	41.9 (37.1-47.4)	16.1 (15.1-17.1)
Cu	251.1 (239.1-263.8)	1146.9 (1048.6-1254.4)	446.6 (423.9-470.6)
Fe	211177.4 (203779.4-218844.0)	1225721 (1160321.7-1294807.2)	275053 (264380.9-286157.6)
Hg	8.3 (7.9-8.8)	49.4 (46.2-52.9)	4.99 (4.73-5.27)
Pb	130.0 (125.2-134.9)	682.0 (630.4-737.8)	344.1 (324.5-364.9)
Zn	872.1 (842.9-902.3)	3938.3 (3718.2-4171.4)	1503.4 (1415.2-1597.1)
PAHs	16.1 (15.1-17.2)	37.3 (31.2-44.5)	113.6 (105.4-122.4)
PCBs	0.19 (0.18-0.20)	0.43 (0.37-0.50)	1.13 (1.04-1.22)

3.4 - Discussion

This study applied a combination of approaches that included regional assessments, local statistics (Getis-Ord analysis) and mass balance estimates in order to provide an assessment of spatial/temporal patterns of priority pollutants in sediments of the Huron-Erie Corridor. A similar assessment was performed for the Detroit River in isolation as described by Szalinska et al. (2013). Given that the present research and that of Szalinska et al. (2013) utilized portions of the same data sets, overall patterns observed for the Detroit River were generally similar with that previously reported. The Szalinska et al. (2013) dataset compared the 1999 survey to the 2008/09 survey and identified that through time the system was remaining stable with respect to concentrations. They also identified that the sampling resolutions were different not allowing a good geospatial comparison. The current study combined the 2008/09 60 sampling stations with the 76 stations from the 2013 survey bolstering the sampling resolution to 136, compared to the 150 in the 1999 survey, allowing for a more direct comparison of early and late time periods on the same spatial scales. Overall the late dataset corresponded with the 2008/09 with no significant differences observed between the Szalinska et al. 2013 study, except for the fact that some sampling locations in the 2013 study were found to contain the highest recorded concentrations with respect to multiple contaminants (Hg, Fe, PAHs).

The U.S. side of the Detroit River was significantly more contaminated with respect to Group 1 chemicals and Hg. The Getis-ord maps help to show these patterns that focus on areas such as downstream of Conner's Creek, River Rouge and the most

extensive contamination with in Trenton Channel and its downstream waters. The contamination on the U.S. side of the Detroit River was identified in the early 1970's and has been heavily studied with many remediation activities taking place in this region of the AOC (Besser et al., 1996; Hamdy and Post, 1985; Marvin et al., 2004a; Zarull et al., 2001). Following identification, considerable emphasis has been placed on minimizing the input of PCBs, PAHs and metals into the Great Lakes with over 130$ million U.S. dollars spent on remediation between 1993 and 2001 with ten remediation projects. Detroit River remediated zones include Conner's Creek (2004 sediment removal) in the upstream Detroit River, the Carter Industrial Site (1995-1996) located closely to the ambassador bridge, and the BASF riverview property (2004 watertight barrier walls), Monguagon Creek (1997), Black Lagoon (2004 sediment removal) and the Elizabeth Park Marina(1993) all within the Trenton channel (see Fig 1,Hartig et al., 2004). It has been demonstrated that significant decreases in concentrations of specific areas of the river occurred from the 1970's to 1990's (Besser et al., 1996; Jia et al., 2010; Marvin et al., 2004b) but insufficient data have been unable to show significant decreases since then and the need for both localized and large scale monitoring was identified as one of the management lessons learned from the remediation activities that took place (Hartig et al., 2004). This study failed to identify significant changes both on localized and broad scales with respect to Group 1 and Hg contamination in the Detroit River, only demonstrating a change with respect to HCB and OCS through time. Notably the sediment remediation activities that took place between the early and late time periods failed to contribute to significant changes with respect to regional wide concentration

decreases. Furthermore, these same areas continue to be identified as the designated hot zones by the Getis-ord analysis indicating that though they remain stable through time.

Both the St. Clair River and Detroit Rivers are designated AOC's but were found to have significantly different patterns of contamination. The Detroit River contained the greatest number of PEC exceedances, the highest geometric mean values for each contaminant, and the largest hot zone regions for selected contaminants. The St. Clair river was found to be the second most contaminated system for group 1 chemicals compared to Lake St. Clair, however Lake St. Clair was more contaminated with respect to Hg then the St. Clair River. The use of Getis-Ord hot and cold zone interpolation maps helped narrow localized areas where contamination is most extensive and place these patterns into a corridor-wide perspective. Within the St. Clair river, hot zones are highly localized for HCB and Hg and elevated on a relative basis in a small section covering only 2% of the Canadian midstream reach in the vicinity of Stag Island. This region has previously been identified as a zone of mitigation in other research dating back to 1974 (Mudroch and Hill, 1989; Thomas, 1974). This area from the 1970's observed significant concentration between the 1970's and 1990's (Marvin et al., 2004a; Richman and Milani, 2010) due to extensive remediation activities. But similar to the Detroit River, significant concentration decreases since the 2000's has failed to be observed for Hg. However, HCB showed a decreasing trend within the zone of mitigation, but has been found to remain more stable further downstream from the zone of mitigation (Richman and Milani, 2010; Szalinska et al., 2007).

In Lake St. Clair a large central hotspot region for Hg only was identified in which its concentrations were significantly more contaminated on the Canadian side of the Lake. This corresponding to historical trends which identified the highest concentrations to be found in the central and east-central areas representative of the deepest parts of the lake excluding the dredged shipping channel (Mudroch and Hill, 1989; Thomas, 1974). These trends were identified throughout the 2000's (Forsythe et al., 2016; Gewurtz et al., 2007; Marvin et al., 2004a) with again previous reports of decreasing trends between the 1970's and 2000's but with no significant changes apparent from 2004 onward.

This study helped to identify another shortfall that was observed by (Szalinska et al., 2013) with respect to sampling resolution between sampling time periods. The identification of sampling density differences between the early and late time periods in the St. Clair River was found to play a significant role in the regional mean, along with the location of hot and cold zones. If both corridor wide surveys had equivalent sampling resolution the temporal comparison would be stronger, particularly for the St. Clair River and Lake St. Clair. By combining the 2013/2008-09 data sets for the Detroit River, these artifacts were less apparent (150 vs 136 sampling stations in early vs late periods) with the same spatial distributions allowing for sampling distributions to not play a major role in effecting results of the analysis. Sampling constraints like this are commonly identified due to logistical and financial constraints associated with high analytical costs.

For the Detroit River, sampling resolution on the order of 136 stations appeared to generate consistent local patterns suggestive of stabilized sediment chemistry as previously concluded by Szalinska et al. (2013). However, the sensitivity of geospatial approaches implemented in the present research will be both system and contaminant specific. System characteristics that appear to impact sample density requirements include the degree of system heterogeneity with respect to depth regimes and heterogeneity of sediment characteristics that impact sediment sorption capacity. Contaminant specific characteristics that impact sample density requirements also include the diversity and positions of sources. Both Hg and HCB in the St. Clair River had high heterogeneity with respect to sediment contamination necessitating higher sampling resolution compared to PCBs for this AOC.

Future studies designed to validate hot and cold zone delineations identified in this research are encouraged, particularly with respect to hot zones and delineation of potential remediation activities. Lastly, cold zones identified throughout the HEC could potentially serve as reference sites for evaluating sediment-linked BUIs such as degraded benthos (McPhedran et al., 2016) or restrictions on dredging activities. The combination of observed trends within the corridor allows for both localized and regional evaluation of sediment contamination from which other research can benefit overall. This study shows through a combination of hot zone and mass balance analysis that targeted remediation within the HEC is warranted and could lead to improvements in ecosystem health.

3.5 – References

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CHAPTER 4 – GENERAL CONCLUSIONS

The purpose of this thesis was to conduct a geospatial analysis of priority pollutants in the Huron-Erie corridor in order to evaluate if the system is showing changes with respect to priority contaminants in sediments of the system. The importance of evaluating two AOC's, the St. Clair River and Detroit River, along with Lake St. Clair with respect to multiple contaminants and comparative techniques, along with new spatial approaches is key to understanding how the system is changing and if the AOC's are showing improvements with time. Large scale probability based sediment surveys throughout the Huron-Erie Corridor using a random-stratified sampling approach that were completed since 1999, along with the most recent 2013-2014, provided a comprehensive database to allow for a number of spatial and temporal comparisons that were addressed in the chapters which are summarized below.

4.1 - Chapter 2

Chapter 2 of this thesis investigated and evaluated the most appropriate technique for using the Getis-Ord statistic in the Huron-Erie corridor, which had been only once previously applied to the corridor in the Detroit River. Three approaches were tested, a fixed distance approach, which was previously used in the Detroit River (Szalinska et al., 2013), an inverse distance weighting approach, and a user defined matrix approach, which considers hydraulic and island barriers. Mercury contamination data was used to test each of the respective approaches. It was anticipated that the fixed distance approach would be the least accurate approach closely followed by the

inverse distance, while the user-defined matrix approach would be the most accurate in its representation of Hg hot and cold zones within the HEC.

The three Getis-Ord approaches were compared with respect to their sensitivity, generated spatial maps and by validation against reserved (independent) validation data sets. Each of the three approaches produced different boundaries of major hot and cold zones within the corridor. Based on validation contrasts, the inverse distance method was found to be slightly more accurate (but non-statistically so) than the user defined matrix. Both the latter methods were more accurate, particularly for hot zone delineation than the fixed distance approach. However, weight of evidence, generated by comparing spatial patterns from each of the three techniques with literature described patterns in the corridor favored the user define matrix approach above the inverse distance weighting method. Therefore, the hypothesis that the user defined matrix approach was the most appropriate Getis-Ord method for use in describe sediment contamination within the HEC was accepted.

4.2 - Chapter 3

Chapter 3 of this thesis provided a temporal assessment of multi-pollutant sediment contamination at the Huron-Erie corridor scale. Focusing on regional, local and temporal assessment techniques the database of sediment contamination from 1999-2014 was compiled and evaluated to test whether changes in the magnitude and location of priority contaminants in sediments has occurred and whether similar patterns of change are apparent across multiple contaminant groups. The main hypothesis tested was that contamination will have decreased in specific reaches of the

corridor such as the Detroit River U.S. side and St. Clair River Canadian side due to remediation activities and the improvement of legislation and activities to help mitigate current sources. It was expected that zones of low contamination will remain relatively stable as previous studies have shown (Szalinska et al., 2013).

The combination of PCA analysis, Getis-ord hot and cold zone identification, and mass balance estimates were able to portray distinct patterns of sediment contamination throughout the Huron-Erie corridor. All chemicals including PCBs, PAHs, select OCs, major priority metals HCB and Hg all exhibited strong spatial contamination patterns with significant concentration differences occurring between both countries and waterbodies. The U.S. side of the Detroit River was the most contaminated zone for all Group 1 chemicals, and exhibiting high Hg and HCB concentrations. The St. Clair River zone of mitigation proved to still contain high concentrations of Hg and Group 2 chemicals including HCB and OCS.

With time, each respective country-waterbody zone (e.g. – U.S. side Detroit river) demonstrated that there was no significant changes in concentration observed through time for Group 1 chemicals. HCB however demonstrated with time a significant decrease for the Detroit River and U.S. side of both Lake St. Clair and the St. Clair River. Mercury was evaluated as a separate chemical due to its number of Probable Effect Concentration (PEC) sediment quality guideline exceedences in each of the respective waterbodies as well as its historical contamination in reaches of the corridor. Mercury within each respective country-waterbody zone exhibited no changes through time except for a small unique zone within the Walpole delta and an apparent decrease in

concentrations in the U.S. portion of the St. Clair River. Overall, the chapter 3 hypothesis was rejected based upon the majority of contaminants not showing significant decreases in concentration over time in hot zones with the exceptions being specific hot zones for HCB and OCS and Hg, the latter being attributed to sampling resolution deficiencies in the early year time period.

4.3 – Conclusions and Future Research

Overall this thesis helped to identify important contaminant trends in the Huron-Erie Corridor through time and space. Chapter 2 was able to identify limitations of commonly applied spatial interpolation techniques related to the application of Getis-Ord analysis. Validation exercise strongly discriminated against the fixed distance method which is the default software parameterization and which was previously utilized in studies on sediment contamination of the Detroit River (Szalinska et al. 2013). Thus, the analysis generated in Chapters 2 and 3 on Hg and priority contaminant hot and cold zone localization supersedes the previously published patterns and is considered more accurate in its representation of hot and cold zones in the corridor.

The institution of the Getis-Ord hotspot analysis in Chapter 3 along with PCA analysis, and mass balance estimates allowed a comprehensive identification of localized and regional scales of priority contaminant distributions. This research expanded upon focused point source tracking studies within the AOCs generated since the 1960s, but provided a unique comparison at the corridor-wide scale. Large scale temporal improvements in sediment quality within the HEC were not apparent over the early time period (1999-2005) to late period (2008-2014) data sets for Group 1

chemicals and Hg, but some evidence of temporal changes of HCB were apparent. Mass balance exercises demonstrated that major hotspots for PCBs and Hg contained a greater proportion of chemical mass relative to the proportion of area represented by the zone within either the AOC or HEC. This provides support for continued efforts to clean-up localized hotspots given that activities of this type can significantly change the surface sediment mass balance and therefore likely yield tangible benefits to BUIs at the corridor scale. Another important observation generated via Chapter 3 was the identification of large scale cold zones in the AOCs and Lake St. Clair. These cold zone areas could be of benefit for use as reference areas when comparing BUIs relative to localized hot zones in the corridor.

This study used an approach appropriate for the assessment of both regional and local contamination. This approach differs from the original studies which instituted the point source tracking method that often misrepresented the health of the entire system. Future studies and research in areas of concern should learn from the history of assessment throughout the Huron-Erie Corridor. The stratified random sampling approach applied in this research could have provided key insight at both regional and localized scales if it were performed before the localized point source tracking studies. Newly studied systems or branches of research focusing on an area for the first time should learn and adopt the techniques of the random stratified sampling strategy as a first step in order to establish a baseline understanding of regional patterns and localized characteristics. These updated sampling designs provide a better understanding of what is happening within a given system better then focusing on point

source zones. Point source areas, identified through the first general survey can be then contrasted with clean areas within the system and/or then focused on with the greater understanding of the system being evaluated.

Future studies should aim to test and validate the hot and cold zones demonstrated by the Getis-ord user defined technique as a means of further discriminating between the inverse distance and user defined matrix approach. This would necessitate targeted sampling at the hot and cold zone boundaries generated by the two methods to further discriminate between them. If a future sampling protocol was able to contain 100 points, areas such as the Trenton channel hotspot extending all the way through the Canadian side, the Lake St. Clair hotspot expanding into the cold region, and then midstream St. Clair River hotspot encompassing both the U.S. side and the Canadian side should be inclusive of an equal number of evenly spaced sampling points (gridded approach) on a roughly 250m to 300m scale in order to give the most accurate representation of border zones of the respective hotspots. These should encompass both nearshore and channelized areas if sample grabs are able to be obtained. The dispersion of the gridded sampling points extending to the largest areas given on maps of the Fixed Distance and User defined matrix will help to further test and define accuracy of these locations, further validating that the User defined matrix was the appropriate selection. Higher resolution sampling of these zones based upon a gridded approach would be feasible due to only three main zones being thoroughly tested throughout the corridor.

4.4 - References

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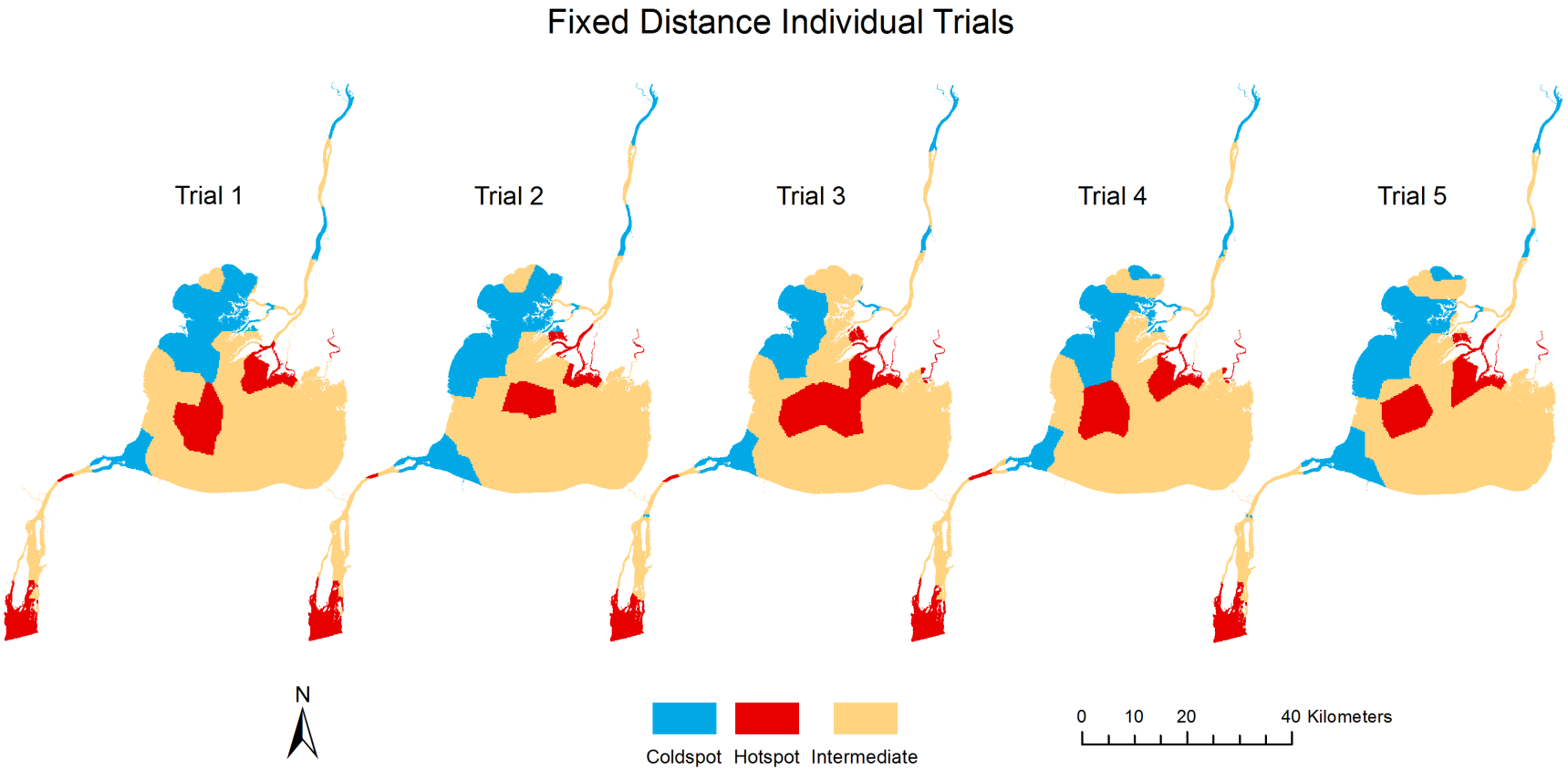
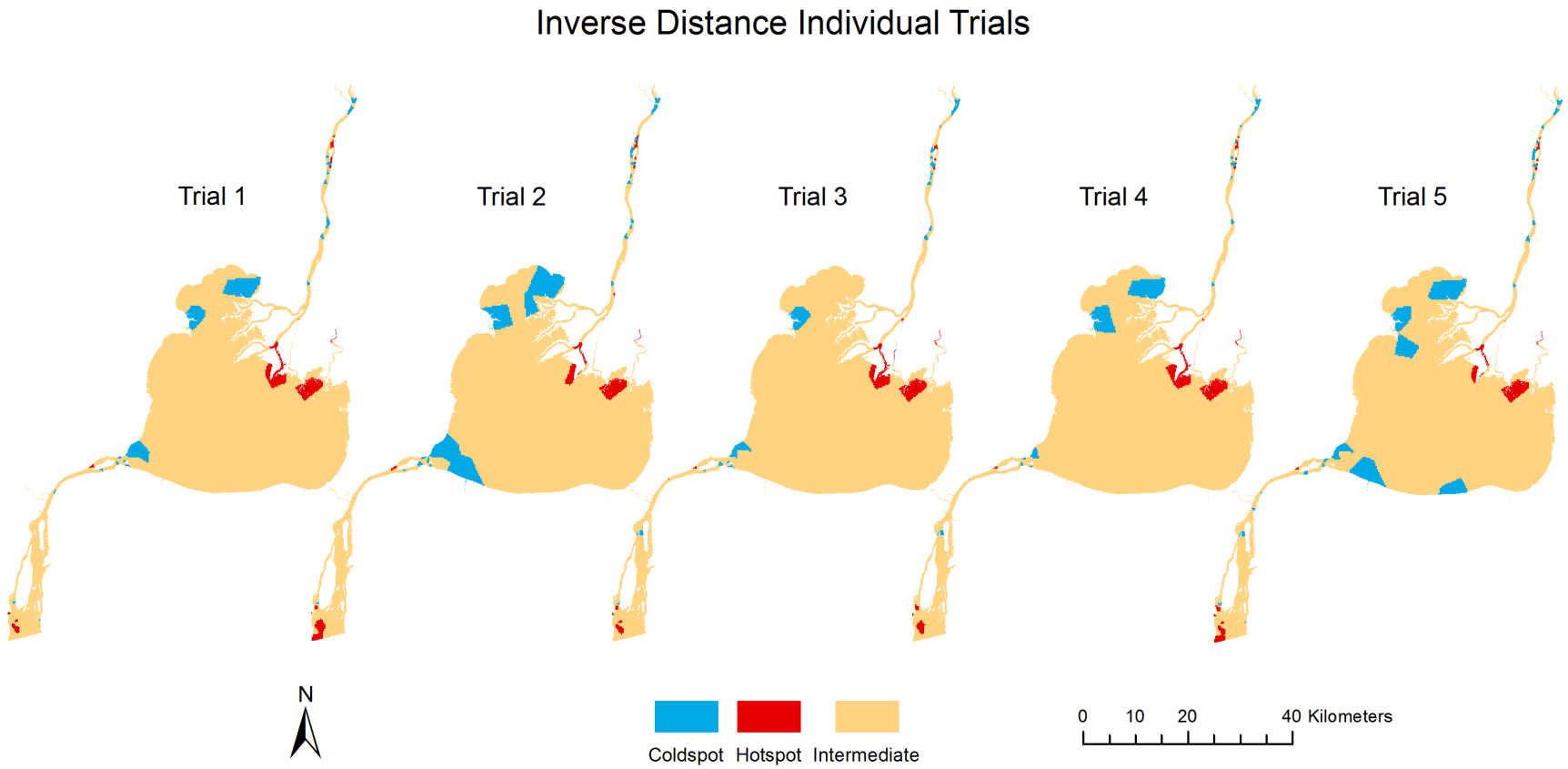
APPENDIX

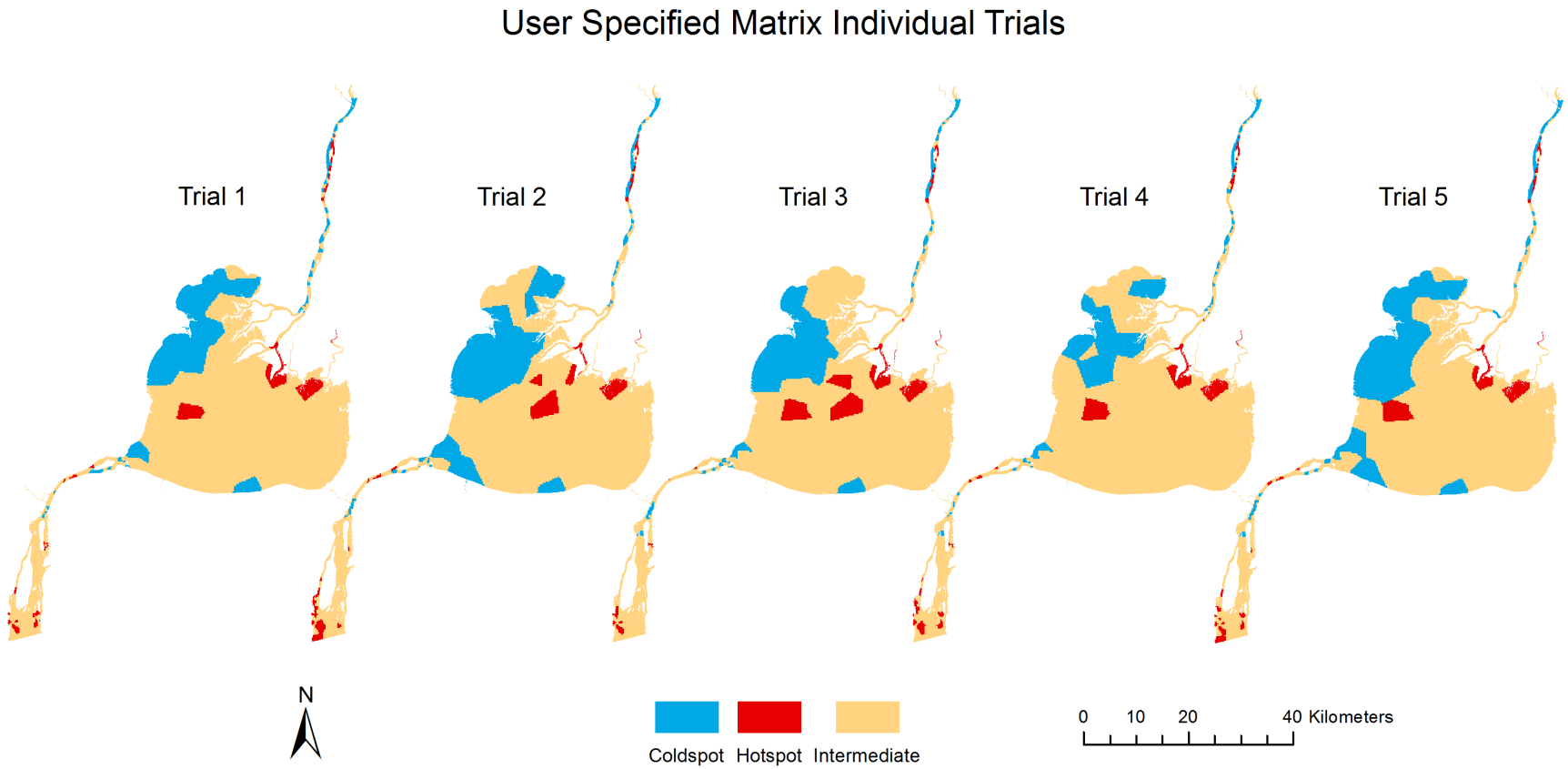
See next page for Appendix 1 - 4



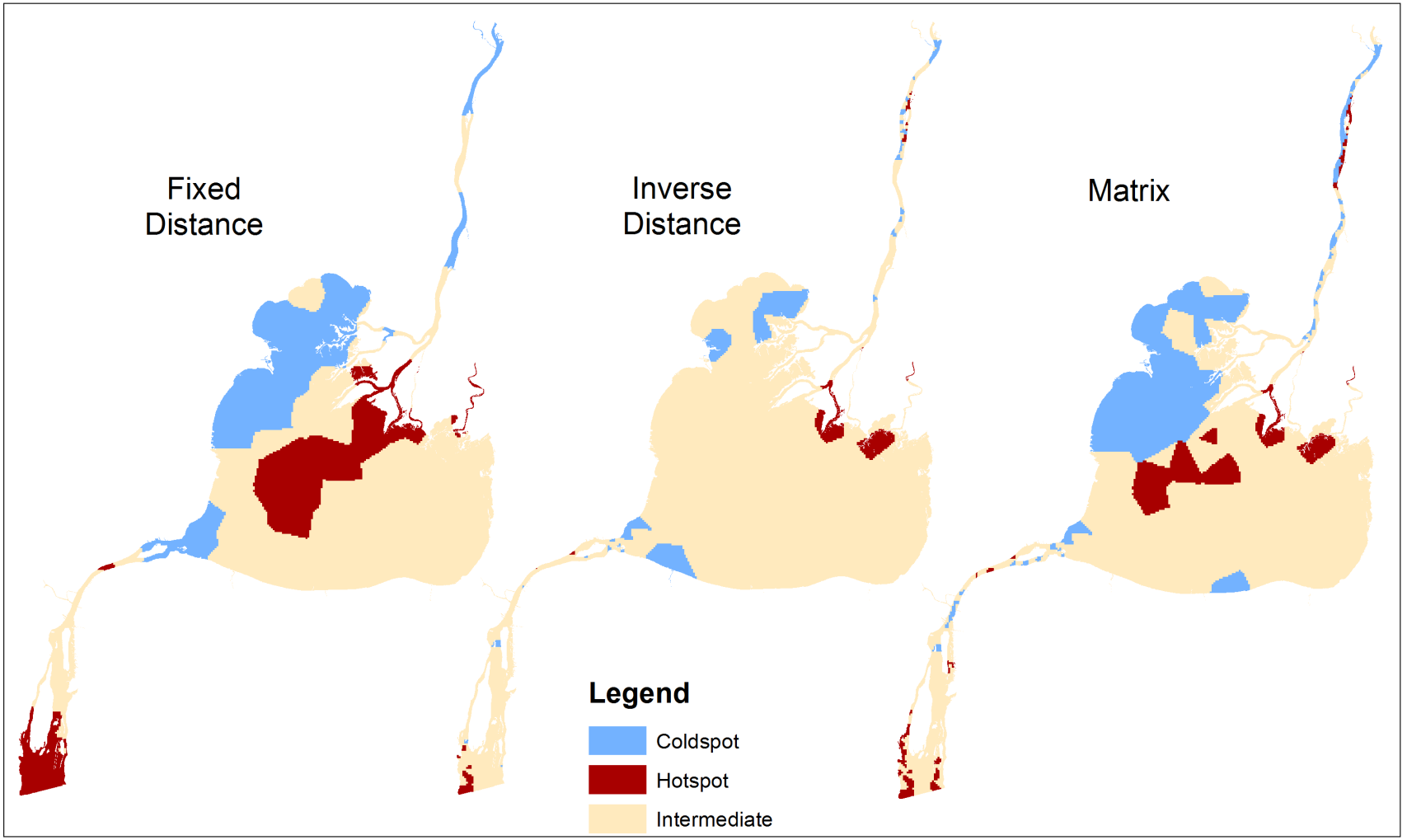
Appendix 1 Trials areal comparison maps for the Fixed Distance Method



Appendix 2 Trials areal comparison maps for the Inverse Distance Method



Appendix 3 Trials areal comparison maps for the User defined Matrix Method



Appendix 4 Method comparison inclusive of all sampling locations

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